REACTIONS RELATED TO OXIDATIONS

by

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ABSTRACT OF THESIS

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Title of Thesis Reactions Related to Oxidations

Mixtures of methane, ethane, propane, cyclopropane, isobutane, and neopentane have been reacted with molecular oxygen in a static system between 325° and 495° C. The residual alkanes were estimated by gas chromatography, and the relative rates of hydrocarbon consumption by the chain-propagating radical X in reactions (1) and (2)

$$R_aH + X = R_a + XH \qquad (1)$$

$$R_bH + X = R_b + XH \qquad (2)$$

were calculated from the equation:

$$\frac{k_a}{k_b} = \frac{\log [R_aH]_{initial} - \log [R_aH]_{final}}{\log [R_bH]_{initial} - \log [R_bH]_{final}}.$$

The relative rate constants found were independent of total pressure and relative hydrocarbon concentrations, and varied only slightly with temperature. A marked variation of rate constant ratios with the oxygen to hydrocarbon ratio was observed.

Alkylperoxy radicals have been generated in mixtures of methane, ethane, propane, cyclopropane, isobutane, n-butane, neopentane, and propylene between 145° and 230° C by the photolysis of symmetric ketones in an excess of oxygen. The relative rates of consumption of these hydrocarbons by reactions (3) and (4)

$$R_aH + ROO = R_a + ROOH \qquad (3)$$

$$R_bH + ROO = R_b + ROOH \qquad (4)$$

have been calculated from the equation above. The relative rate constants were found to be independent of reactant concentrations, illumination time, and total pressure, and to be almost independent of temperature and of the alkylperoxy radical attacking the hydrocarbons.

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The following general characteristics of hydrocarbon oxidation have been deduced from the experimental evidence and the literature cited. Below 250° C, oxidation appears to occur by a non-chain attack by alkylperoxy radicals. In the temperature range of thermal oxidation, a chain propagated by HO_2 radicals is responsible for hydrocarbon attack, and explains the large yields of olefin formed. At temperatures above 350° C, a second chain, possibly propagated by OH radicals, consumes increasing amounts of hydrocarbon as the reaction advances. This second chain may eventually displace the HO_2 radical chain.

The relative rates of attack at different points in paraffins by alkylperoxy radicals and by the chain-propagating radical in the initial stages of oxidation have been calculated from the experimental data. The radical reactivities are found to be similar. Initial attack occurs at tertiary bonds in preference to secondary, and at secondary in preference to primary. Cyclopropyl C-H bonds are about eight times less reactive than normal secondary bonds; methyl C-H bonds are at least ten times less reactive than normal primary bonds at 230° C.

An activation energy of 3-8 kcal $mole^{-1}$ has been found for the abstraction of a hydrogen atom from a saturated hydrocarbon by an alkylperoxy radical; the value for HO_2 abstraction should be similar. As these small absolute activation energies would suggest, the activation energy differences between abstraction reactions from various hydrocarbons are found to be small.

THE UNIVERSITY *of* EDINBURGH

To the memory of

WILLIAM JULIUS SCHADEK

and

CONDREN ALVIN CHARLES SCHADEK

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PREFACE

The object of this research was to elucidate the nature of the chain-propagating reactions responsible for the main consumption of hydrocarbon in the gas phase oxidation of saturated hydrocarbons, and to determine the nature of the radical responsible for hydrocarbon attack. Two closely related groups of experiments have been performed :

(1) The relative rates of consumption of mixed alkanes oxidized with molecular oxygen have been measured by a simple competitive method. The nature of the attacking radical, X, is unknown, but certain deductions can be made about its properties, and its behaviour can be compared with that of likely chain-propagating radicals, eg. OH, HO_2, RO, and RO_2.

(2) The relative rates of consumption of alkanes by one class of oxygenated radicals, alkylperoxy, have been determined, and the reactivities of these radicals have been compared with those of radical X.

This investigation was undertaken because there is little agreement among current theories of low temperature hydrocarbon oxidation as to either the basic chain-propagating steps or the identity of the chain-propagating radical. Furthermore, little data concerning transfer reactions involving relatively simple oxygenated radicals is available.

The general background to the problem and the approach that has been employed here are discussed in the introduction. Following a description of the experimental apparatus and techniques, results are presented for the two groups of experiments performed. Results for a number of oxidations of ethane, ethylene, and propylene obtained in the course of the study are included. The significance of the results is explained in the discussion. The conclusions drawn from the investigation form the final chapter of the thesis.

The conventions and nomenclature used throughout this thesis are given in Table 1.

TABLE 1

CONVENTIONS AND NOMENCLATURE

A = A factor
E = Activation energy } Arrehenius parameters
T = Absolute temperature
t^{o} = t degrees Centigrade
k_a = rate constant for hydrocarbon R_aH
R = alkyl radical
R = gas constant
[X] = concentration of X
ΔH = enthalpy of reaction
D(A-B) = dissociation energy of bond A-B

INTRODUCTION

1. GENERAL INTRODUCTION

The earliest recorded investigations into the field of hydrocarbon oxidation were made by John Dalton[1] in 1803-4, when he investigated the partial combustion of methane and ethylene, the only hydrocarbons recognized as such at that time. Although his experiments showed that the principal products in ethylene oxidation were carbon monoxide and hydrogen, it was maintained throughout the first half of the nineteenth century that in a hydrocarbon oxidation hydrogen was oxidized first, and carbon attacked at a later stage. This view was finally overthrown due to the efforts of Kersten[2] and others who held the opposite extreme to be true, that is, that all the carbon was oxidized to carbon monoxide before any of the hydrogen was attacked.

These extreme views were replaced around the turn of the century by the principal forerunner of the modern theories of combustion, the Hydroxylation Scheme which was first proposed by Armstrong[3] in 1874, but principally expounded by Bone[4] and his colleagues. This theory was of great importance because it incorporated the fundamental concept of a stepwise reaction, the keystone of subsequent theories.

Since the decline of the hydroxylation theory, current theories explaining the slow oxidation of hydrocarbons in the gas phase have been based upon a degenerately branching free-radical chain mechanism[5]. The reaction chains are straight and of finite length. Their products include certain intermediates which react after an interval, long in comparison to the life-time of the straight chain, to initiate new chains. The reaction will accelerate exponentially if each chain produces, on the average, sufficient branching intermediate to initiate more than one new chain.

Studies of hydrocarbon oxidation ranging from the measurement of antiknock to the rates of slow oxidation have shown that the reactivity of hydrocarbons towards oxygen is greatly dependent upon their structure. Lengthening the hydrocarbon chain increases the reactivity of a hydrocarbon but branching of the hydrocarbon chain lowers the reactivity. Cullis, Hinshelwood, and Mulcahy[6,7] measured the differences in reactivity roughly by determining the rates of pressure rise in the oxidation of pairs of hydrocarbons under the same conditions. The reactivity varied widely and they were forced to use different conditions of temperature and pressure for each pair. Since the relative reactivity of any pair will depend upon the conditions, this method of comparison of oxidisability gives only qualitative results. Cullis and Hinshelwood[6] recognised that the differences in reactivity resulted from differences in the rates of several characteristic processes, for example, chain initiation, propagation, branching, etc., rather than of a single process. In order to discover the source of such differences, methods of isolating the various contributory factors must be found.

It is generally agreed that the first products to be formed from a hydrocarbon molecule undergoing oxidation are alkyl radicals formed by hydrogen abstraction. Most hydrocarbons with three or more carbon atoms form several such alkyl radicals. Insight into the reaction mechanism could therefore be obtained by determining the proportions of these radicals formed by a given hydrocarbon. To do this it is necessary to measure the yields of characteristic products from the different points of initial attack.

Burt, Cullis, Ebeid, Larsen, and Minkoff[8] oxidised deuteropropanes at 423° with 1/5 oxygen-propane mixtures. The relative amounts of OH and OD in the water and hydrogen peroxide formed were determined by infra-red spectroscopy. The results obtained with a number of deuteropropanes showed that the chance of a given secondary hydrogen atom appearing in the hydroxyl groups formed was 2.1 times the chance of a given

primary hydrogen atom appearing, and that for any given position the chance of deuterium appearing in the hydroxyl group was only 0.41 times the chance of hydrogen appearing. The authors interpreted these results as meaning that initial attack at a secondary carbon atom was 2.1 times as probable as attack at a primary carbon atom. This deduction requires the further assumption that it is only the hydrogen atom which is initially abstracted that appears in the water. Therefore it must be assumed that both the hydrogen atoms in the water come from the initial attack. It is virtually impossible to devise a reaction scheme for which this is true. The only plausible reactions whereby water can be formed are :

$$OH + RH \longrightarrow H_2O + R$$

and

$$HO_2 + RH \longrightarrow H_2O_2 + R$$

$$\longrightarrow H_2O + \tfrac{1}{2}O_2 + R.$$

OH can reasonably be formed only by the decomposition of some other oxygenated free radical at temperatures as high as 423°. It is highly unlikely that the reaction

$$O + RH \longrightarrow OH + R$$

occurs in normal oxidations at 400°, and

$$ROOH \longrightarrow RO + OH$$

cannot be important above 400°. The hydrogen atom in OH will almost certainly not come from the point of initial attack, unless RO_2 undergoes a very unusual elimination reaction. The position with HO_2 is similar. It is now generally accepted that the oxidation of propane in the early stages at temperatures above 400° occurs by an HO_2 radical chain which forms propylene as one of its other major products[9,10]. Thus one hydrogen atom arises from the primary and the other from the secondary position irrespective of where the initial attack occurs. Therefore, in the early stages of the reaction the probability of a given

secondary hydrogen atom appearing in the water or hydrogen peroxide is expected to be three times that for a given primary. However, by the time that about 20 per cent of the propane is consumed (oxygen and propane are consumed at roughly the same rate at 420°), considerable secondary oxidation has occurred as can be seen clearly from the results of Falconer and Knox[9]. The fact that 0.6 of the hydrogen in the water comes from the ends of the molecule rather than the expected one-half implies that the organic oxidation products contain more than their statistical share of hydrogen from the centre of the molecule. Unfortunately these results give virtually no information about the point of initial attack.

Braude, Cullis, Hardy, and Turner[11] determined the points of origin of the carbon monoxide and ketones from the oxidation of ^{14}C labelled 2-methyl pentanes (isohexanes) and assumed that the relative yields of carbon monoxide and carbonyl from any position in the isohexane molecule gave the point of initial attack on the hydrocarbon. Experiments were carried out at 242° with mixtures of 200 mm isohexane and 100 mm oxygen. Their assumption is open to serious criticism. They assume that the alkyl radicals formed initially from the hydrocarbon are converted entirely into the hydroperoxide with the OOH group attached to the point of initial attack. They then assume that primary and secondary hydroperoxides decompose to form carbon monoxide in roughly equal proportions and that the tertiary hydroperoxides give little carbon monoxide but an equivalent amount of ketone. The yield of carbon monoxide and carbonyl is thus assumed to give the amount of initial attack at any carbon atom. The decomposition of ethyl, isopropyl, and t-butyl hydroperoxides has been studied by Kirk and Knox[12]. The homogeneous decomposition yields an alkoxyl and hydroxyl radical. The alkoxyl radicals decompose to carbonyl compounds and alkyl radicals. The yield of carbonyl will therefore give a measure of the peroxide from which it is formed, and the carbonyl group is where the OOH group was previously. Carbon monoxide is, however, likely to arise from the oxidation of a methyl radical or from

heterogeneous decomposition of the peroxide. In neither case will the carbon atom in the carbon monoxide necessarily be that at which initial attack occurs. In the experiments of Kirk and Knox[12] it was generally found that the yield of carbon monoxide was not more than 10 per cent of that of the peroxide decomposed at temperatures below 300°, but that all types of peroxide gave roughly the same proportion of carbon monoxide. It is highly improbable that the per cent yield of carbon monoxide from primary and secondary hydroperoxides is the same as the per cent yield of ketone and carbon monoxide from a tertiary hydroperoxide, and it is unlikely in any case that the carbon monoxide formed arises from the carbon atom initially attacked in the parent hydrocarbon. Thus the interpretation of the ^{14}C work of Cullis, Hardy, and Turner[11] is invalid.

While Minkoff, Cullis, and co-workers[8,11] have attempted to measure the relative rates of initial attack by the "product method", they have not been able to select products that are characteristic of the point of attack. Their method could give reliable results only if the mechanisms of oxidation of the hydrocarbons were much better understood. There is, therefore, no direct information on the relative rates of attack in oxidations at different points in the same hydrocarbon molecule.

Knox, Smith, and Trotman-Dickenson[13] indirectly estimated the rates of attack at different points in hydrocarbons by determining the effect of structure on the relative rates of consumption of two hydrocarbons, R_aH and R_bH, in a mixed oxidation. The rate constant ratios, k_a/k_b, were determined using the competitive method described on page 8 of this thesis. The oxidation of propane-ethane and propane-isobutane mixtures, first studied in the way[13], showed k_a/k_b to be independent of the relative hydrocarbon concentration, the total pressure, and the oxygen concentration, and to be almost independent of the temperature between 274° and 495°. Part of this thesis[a] constitutes an extention of their work. It substantiates most cf their findings, but experiments performed at high oxygen concentrations

have revealed a dependence of k_a/k_b upon oxygen concentration above 328°. These results[13,a] show that the reactivities of the chain-propagating radicals derived from different hydrocarbons are identical, but that the chain mechanism changes with the extent of reaction at temperatures above 400°.

Among the many reaction schemes proposed to account for the main features of hydrocarbon oxidation[6,9,10,14,15], there is little agreement as to the identity of the chain-propagating species. Alkylperoxy (ROO·)[6,15] and hydroperoxy (HOO·)[9,10] have been proposed as radicals responsible for chain-propagation, but information on the gas phase reactions of these radicals with hydrocarbons is lacking. Peroxy radicals are well established as chain carriers in the oxidation of aldehydes both in the liquid and in the gas phase[16-18], and in the oxidation of paraffins[19] and olefins[20] in the liquid phase. The remaining part of this thesis describes the reactions of four alkylperoxy radicals with hydrocarbon mixtures[b].

2. THE COMPETITIVE REACTION SCHEMES

A. Competitive Oxidations

Since the basic chain must be mainly responsible for the disappearance of hydrocarbon in an oxidation, the relative rates of the main propagating reactions in a mixed oxidation may be found either by measurement of the relative rates of disappearance of the two hydrocarbons or by measurement of the rates of appearance of characteristic products formed from them. The latter method has the disadvantage that it is not easy to select products that are truly characteristic of each hydrocarbon and which can provide an accurate measure of their disappearance. The former and more direct method has therefore been employed.

In the oxidation of the pure hydrocarbons R_aH and R_bH, the chain-propagating reactions may be written :

$$X_1 + R_aH \xrightarrow{k_{a1}} X_1H + R_a \qquad (1)$$

$$X_2 + R_bH \xrightarrow{k_{b2}} X_2H + R_b \qquad (2)$$

where X_1 and X_2 are oxygenated radicals such as OH, HO_2, RO, and RO_2. When a mixture of the two hydrocarbons is oxidized, two further propagating reactions will occur :

$$X_2 + R_aH \xrightarrow{k_{a2}} X_2H + R_a \qquad (3)$$

$$X_1 + R_bH \xrightarrow{k_{b1}} X_1H + R_b \qquad (4)$$

If we define the overall rate constants for the removal of the two hydrocarbons as k_a and k_b, then the ratio k_a/k_b can be obtained from analysis of the amounts of each hydrocarbon present at the beginning and end of the reaction from the relation

$$\frac{k_a}{k_b} = \frac{\log [R_aH]_{initial} - \log [R_aH]_{final}}{\log [R_bH]_{initial} - \log [R_bH]_{final}} .$$

If $k_{a1} \neq k_{a2}$ and $k_{b1} \neq k_{b2}$, the experimental value of k_a/k_b will depend upon the composition of the mixture.

Oxidations were performed with the individual members of each pair to show that its partner was not a product of its oxidation.

B. Competitive Alkylperoxy Reactions

Symmetric ketones have been photolysed in an excess of oxygen at 145º and 230º to produce alkylperoxy radicals,

$$R_2CO + h\nu \longrightarrow RCO\cdot + R\cdot \qquad (5)$$

$$RCO\cdot \longrightarrow R\cdot + CO \qquad (6)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (7)$$

where R· is $CH_3\cdot$, $C_2H_5\cdot$, iso-$C_3H_7\cdot$, or tert-$C_4H_9\cdot$. At these temperatures, reaction (6) is very rapid for all RCO· except possibly CH_3CO . McDowel and Thomas[17] find some evidence for

$$CH_3CO\cdot + O_2 \longrightarrow CH_3CO_3\cdot$$

at temperatures as high as 200º. Errors introduced by a limited amount of $CH_3CO\cdot$ will be small, however, as Hentz[21] has shown that a similar oxidation sequence exists via $CH_3\cdot$ or $CH_3CO\cdot$ radicals. The addition of an alkyl radical to oxygen, reaction (7), is well established at temperatures below 300º from results obtained in mercury photosensitized hydrocarbon oxidations[22], where large amounts of hydroperoxide were isolated among the products, and photo-oxidations of alkyl radicals[23-30]. Its activation energy[28-30] is probably 0-1 kcal mole^{-1}.

If these radicals are produced in a mixture of two hydrocarbons, R_aH and R_bH , the hydrocarbons are consumed by hydrogen abstractions of the type :

$$ROO\cdot + R_aH \xrightarrow{k_a} ROOH + R_a \qquad (8)$$

$$ROO\cdot + R_bH \xrightarrow{k_b} ROOH + R_b \qquad (9)$$

The relative rate constants, k_a and k_b , of reactions (8) and (9) may be deduced from the equation

$$\frac{k_a}{k_b} = \frac{\log [R_aH]_{initial} - \log [R_aH]_{final}}{\log [R_bH]_{initial} - \log [R_bH]_{final}} ,$$

which is identical to that used to calculate the relative rate constants in competitive oxidations.

This relation is exact only if all the hydrocarbon removed is consumed by the alkylperoxy radical under consideration,

and if the alkyl radicals $R_a\cdot$ and $R_b\cdot$ formed in reactions (8) and (9) react without reforming R_aH and R_bH. In an excess of oxygen, the alkyl radicals formed will react with oxygen rather than abstract from either a ketone or a hydrocarbon to reform the parent. Photolyses performed with each hydrocarbon alone showed that the other member of the pair was not a by-product of the reaction. Trial experiments showed the decomposition of hydrocarbon in the absence of ketone to be negligible. The number of molecules of hydrocarbon consumed never exceeded 0.6 times the number of alkyl (and hence alkylperoxy) radicals generated in the ketone photolysis. Thus the amount of chain reaction is small, and errors in k_a/k_b caused by secondary consumption of hydrocarbon by $R_aOO\cdot$ and $R_bOO\cdot$ will be small unless these radicals have reactivities greatly different from those formed via ketone photolysis. The results presented here show the reactivities of alkylperoxy radicals are virtually independent of the nature of the alkyl radical.

It is also essential that no hydrocarbon be consumed by radicals such as alkyl, alkoxyl, OH, and HO_2 that might be produced in the system. The oxidation of alkyl radicals is rapid compared with alkyl radical abstraction, combination, or disproportionation, because the alkane and dimer corresponding to the ketone used were not present in the reaction products. Furthermore, the reactivities obtained do not correspond to those obtained with methyl radicals[31].

Various reactions have been proposed to convert alkylperoxy to alkoxyl radicals[23,27,32,33]

$$2ROO \longrightarrow 2RO + O_2$$

$$ROO + O_2 \longrightarrow RO + O_3$$

followed by

$$R + O_3 \longrightarrow RO + O_2$$

$$ROO + R \longrightarrow 2RO$$

The reactivities found in the present experiments do not correspond with those found for methoxyl radicals[34], so when R• is CH_3• at least, these reactions do not appear to be significant. Reactivities of other alkoxyl radicals are probably very similar to those of methoxyl, and hydrocarbon consumption by alkoxyl radicals seems unlikely.

Recent results of Bercés and Trotman-Dickenson[35] show that OH is a much more reactive radical than those which attack the hydrocarbon in the present work. Its reactivities at 18° are similar to those of the chlorine atom[36], which it resembles in size and electronegativity.

The most probable reaction giving rise to HO_2 is

$$R + O_2 \longrightarrow \text{olefin} + HO_2 \ . \qquad (10)$$

In the present experiments no olefin was detected in the products, even though the analysis could detect a conversion to olefin of less than 1 per cent of the hydrocarbon consumed. At the present temperatures reaction (10) appears to be unimportant, and it is unlikely that significant quantities of HO_2 are formed.

In view of the above arguments, it seems reasonable to conclude that hydrocarbon consumption under the experimental conditions used here is caused by alkylperoxy radical attack.

EXPERIMENTAL TECHNIQUES

1. MATERIALS

A. Hydrogen, Oxygen, and Nitrogen

Hydrogen, oxygen, and nitrogen were obtained directly from B.O.G. cylinders after passage through a trap immersed in liquid oxygen to remove any condensables, and were stored in two litre bulbs. Analysis showed no hydrocarbon impurities.

B. Hydrocarbons

The hydrocarbons were thoroughly degassed prior to storage in two litre bulbs fitted with traps and blowoff manometers. They were obtained as follows :

Methane - The methane was taken from cylinders after passage through a trap immersed in liquid oxygen to remove condensables. It was distilled between -183° and -208°, the middle fraction only being retained. It was 99 % pure.

Ethane - The ethane used in ethane-cyclopropane and ethane-methane oxidations was passed through a column packed with a mercuric acetate-mercuric nitrate-ethylene glycol solution supported on 20-30 mesh firebrick[37] to remove the ethylene present in the cylinder gas. All other ethane used was freed of ethylene by passing the cylinder gas through sulphuric acid and a column of charcoal saturated with bromine. Bromine vapour and bromides were removed by a 30 % N-N:dimethyl p-toluidene-firebrick mixture. After fractionation, the ethane thus purified contained no detectable impurities.

Propylene - Propylene was prepared by dehydration of A.R. isopropanol with phosphorous pentoxide and was scrubbed with 10 % sodium hydroxide solution. It was then fractionated and the middle fraction retained. No impurities were detected.

Ethylene, propane, cyclopropane, n-butane, isobutane,

and neopentane - These gases were taken from cylinders and fractionated, the middle fractions being retained. They were used without further purification. Chromatographic analysis showed them to be at least 99.5 % pure.

C. Methanol, Acetaldehyde, and Formic Acid

Methanol and formic acid, used as additives in ethane-propane oxidations, and acetaldehyde, used both as an additive and as an initiator is some ethane-cyclopropane oxidations, were A.R. These reagents were vacuum distilled, the middle fractions being retained, and thoroughly degassed prior to use. The formic acid contained some water as an impurity.

D. Formaldehyde and Ketones

Formaldehyde - Monomeric formaldehyde containing no detectable impurities was prepared from 40 % formaldehyde solution by the method of Spence and Wild[38] and was stored in a trap immersed in a dry ice/acetone slush. All surfaces with which the formaldehyde vapour came in contact were maintained above 100º to prevent polymerization.

Acetone and Diethylketone - A.R. acetone and diethylketone were vacuum distilled and thoroughly degassed. No impurities were detected by infra red or chromatographic analysis.

Di-isopropylketone - The di-isopropylketone was a gift from the Shell Chemical Company. After fractionation it was 99 % pure.

Di-t-butylketone - The di-t-butylketone was prepared by the method of Bartlett and Schneider[39], as follows. Sodium sand was prepared in a two litre flask, fitted with a mechanical stirrer, a dropping funnel, and a reflux condensor, by melting 30 g (1.25 mole) of sodium under toluene (250 cc) and stirring until cooled to solidification. The toluene was decanted, and the sand washed three times with n-pentane. Seventy-five cc n-pentane and 75 g t-butylchloride (0.8 mole) were added to the sodium sand,

and 33 g methylpivalate (0.28 mole) were added over one hour with constant stirring. The mixture was refluxed for two hours, and allowed to stand overnight. The resultant green solid mass was treated with 100 cc water. The yellow-green organic layer which separated was distilled. A fraction containing a mixture of di-t-butylcarbinol and di-t-butylketone was collected between 148-163° (21 g). This fraction was refluxed with 60 cc concentrated nitric acid for 30 minutes to oxidize the di-t-butylcarbinol to the corresponding ketone. The organic layer was washed with water, shaken with strong sodium hydroxide solution, washed with water again, and distilled. Fourteen g (0.1 mole) of di-t-butylketone were collected between 153-156° . Its refractive index was $n_D^{20°}$ = 1.4200. Chromatographic analysis showed it to be 95 % pure. The impurities were non-ketonic, and its photolysis yielded no products characteristic of alkyl radicals other than t-butyl.

E. Carbon Dioxide

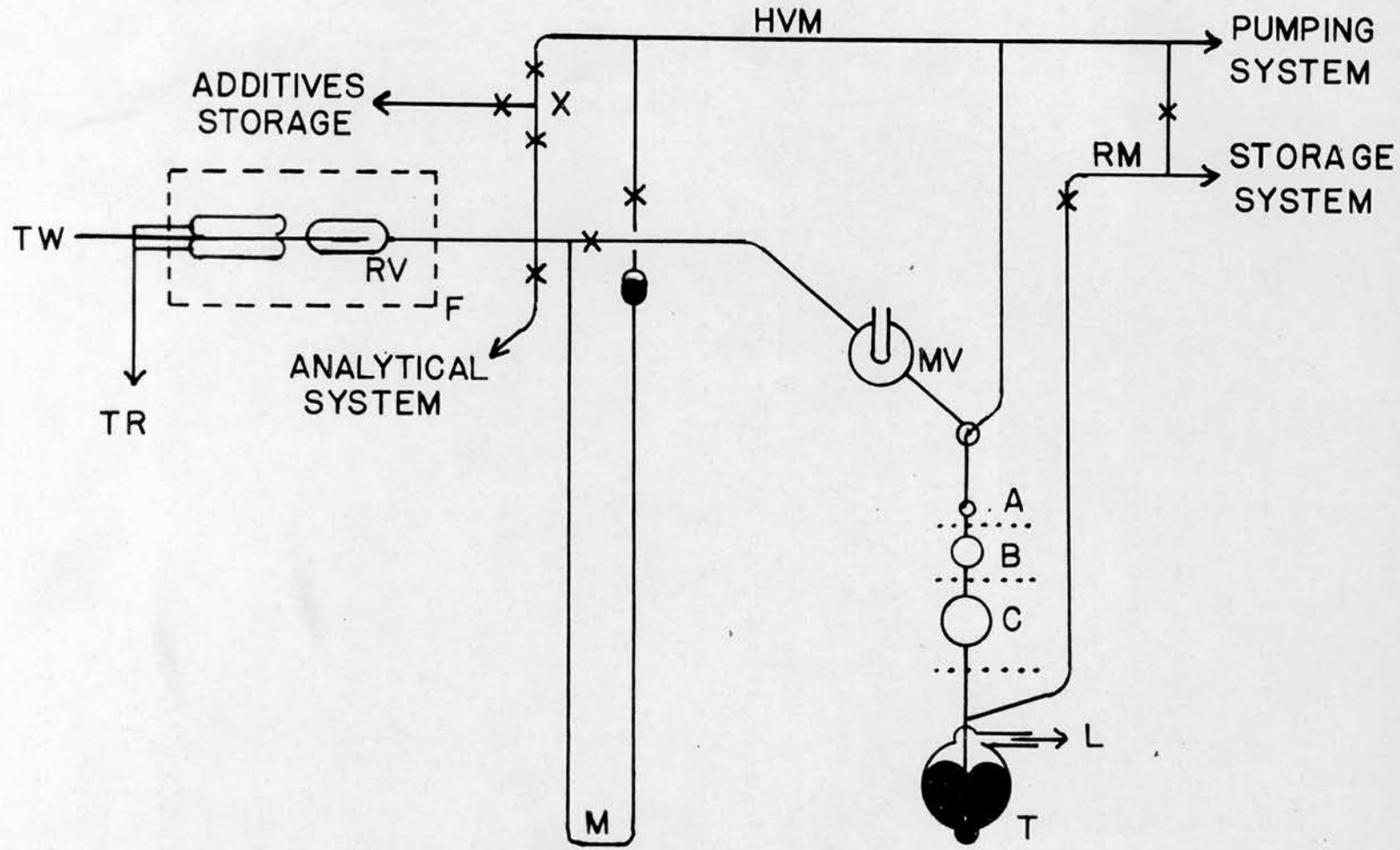
The carbon dioxide used as a carrier gas in the chromatography system was I.C.I. "Drikold", and was used without purification.

2. APPARATUS AND PROCEDURE

A. Kinetic Apparatus for Oxidations

The oxidations were carried out in a conventional static high vacuum apparatus constructed of Pyrex as shown in Figure 1. The high vacuum manifold (HVM) was connected to a pumping system consisting of a two stage all metal mercury diffusion pump backed by a rotary oil pump. The pressure in the apparatus, read on a McLeod gauge, could be reduced to 10^{-5} mm after about 30 minutes pumping.

The volumes A, B, and C of the combination gas burette-Toepler pump (T) were calibrated before being fitted to the apparatus, by weighing the mercury filling each volume. The sections of the burette as shown in Figure 1 had the following volumes :



KINETIC APPARATUS FOR OXIDATIONS

FIGURE 1

$$A = 9.95 \text{ cc}$$
$$A + B = 66.14 \text{ cc}$$
$$A + B + C = 198.53 \text{ cc}$$

The volume of the mixing vessel (MV, 130 cc) and of the reaction vessel (RV, 107 cc) were determined by pressure-volume measurement involving a known amount of gas in the gas burette.

Gases contained in the storage bulbs could be expanded into the gas burette via the reagent manifold (RM). The mercury reservoir was connected to a low vacuum line at L.

The volume of the dead space associated with the reaction volume was minimized by using capillary tubing for all connections made to the reaction vessel and for the manometer (M). The connecting tubing and the manometer were maintained above 80º to prevent condensation. The dead space was approximately $1\frac{1}{2}$ % of the reaction volume.

The reaction vessel was enclosed in an insulated coaxial cylindrical furnace (F), wound in three sections. A temperature gradient along the length of the reaction vessel of less than 1º was obtained by partially shunting the middle section. The furnace temperature was regulated to ± 1º by a gas thermometer type thermo-regulator (TR) and a Sunvic power relay ; it was measured to ± 3º by a single junction T_1/T_2 thermocouple. The thermocouple hot junction was placed in a thermocouple well (TW) coaxial with the reaction vessel ; the cold junction was maintained at 0 ± 1º in crushed ice/water slush. Potential differences were measured on a Croyden potentiometer.

Acetaldehyde and other additives could be admitted directly into the reaction vessel through a stopcock system X. The reaction vessel was also connected to the sampling tube of the analytical system.

B. Procedure for Oxidations

The apparatus was evacuated to 10^{-5} mm. The hydrocarbons were thoroughly degassed. A mixture of hydrocarbons and oxygen

of a predetermined composition was made up in the mixing vessel prior to a series of runs. The individual components were taken from the storage bulbs, accurately measured in the gas burette, and then introduced into the mixing vessel. Liquid oxygen was placed in the cold finger of the mixing vessel to condense some of the gases and enable larger mixtures to be made up.

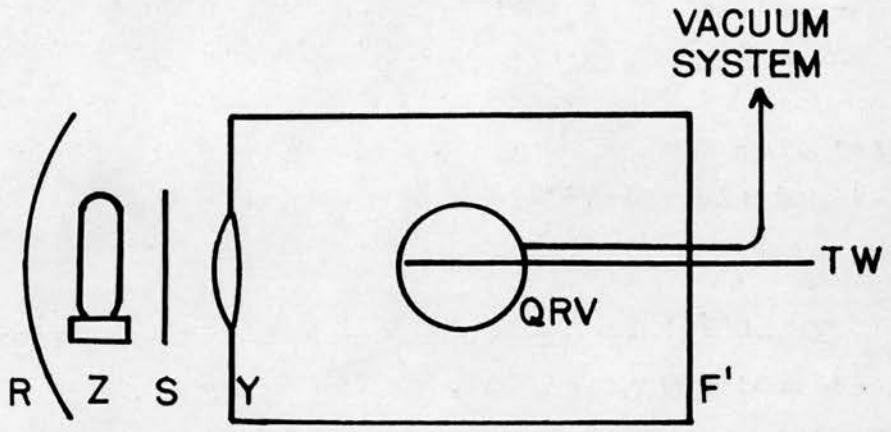
A sample of the mixture was allowed to enter the pre-heated reaction vessel and the initial pressure was measured on the manometer M. The induction period and the reaction period were noted, and after reaction had ceased the final pressure was read. The condensable gases were frozen into a W-shaped sample tube immersed in liquid oxygen for analysis, and the non-condensable gases were pumped through the sample tube to remove remaining traces of condensables. For mixtures containing methane, the W-tube was packed with activated alumina to condense the methane.

C. Kinetic Apparatus for Alkylperoxy Reactions

For alkylperoxy reactions, an apparatus identical to that for oxidations was used with the reaction vessel and furnace changed, and an illuminating system added as in Figure 2.

A 300 cc spherical quartz reaction vessel (QRV), fitted with an axial thermocouple well (TW), was connected to the vacuum system with a Pyrex to quartz graded seal. Dead space (1 %) was minimized as before. The reaction vessel was enclosed in an insulated cylindrical furnace (F') fitted with a quartz lens (Y) at one end. The temperature gradient along the length of the reaction vessel was less than 3°. Temperature was measured by a thermocouple system identical to that used for oxidations.

The reaction vessel was illuminated by the unfiltered light from a 125 watt high pressure mercury vapour lamp (Z) focused by lens Y. A polished aluminum reflector (R) was placed behind the lamp, and an aluminum shutter (S) separated the lamp from the reaction vessel.



REACTION SYSTEM FOR ALKYLPEROXY RADICAL REACTIONS

FIGURE 2

Ketones, formaldehyde, and oxygen could be admitted into the reaction vessel through the series of taps at X.

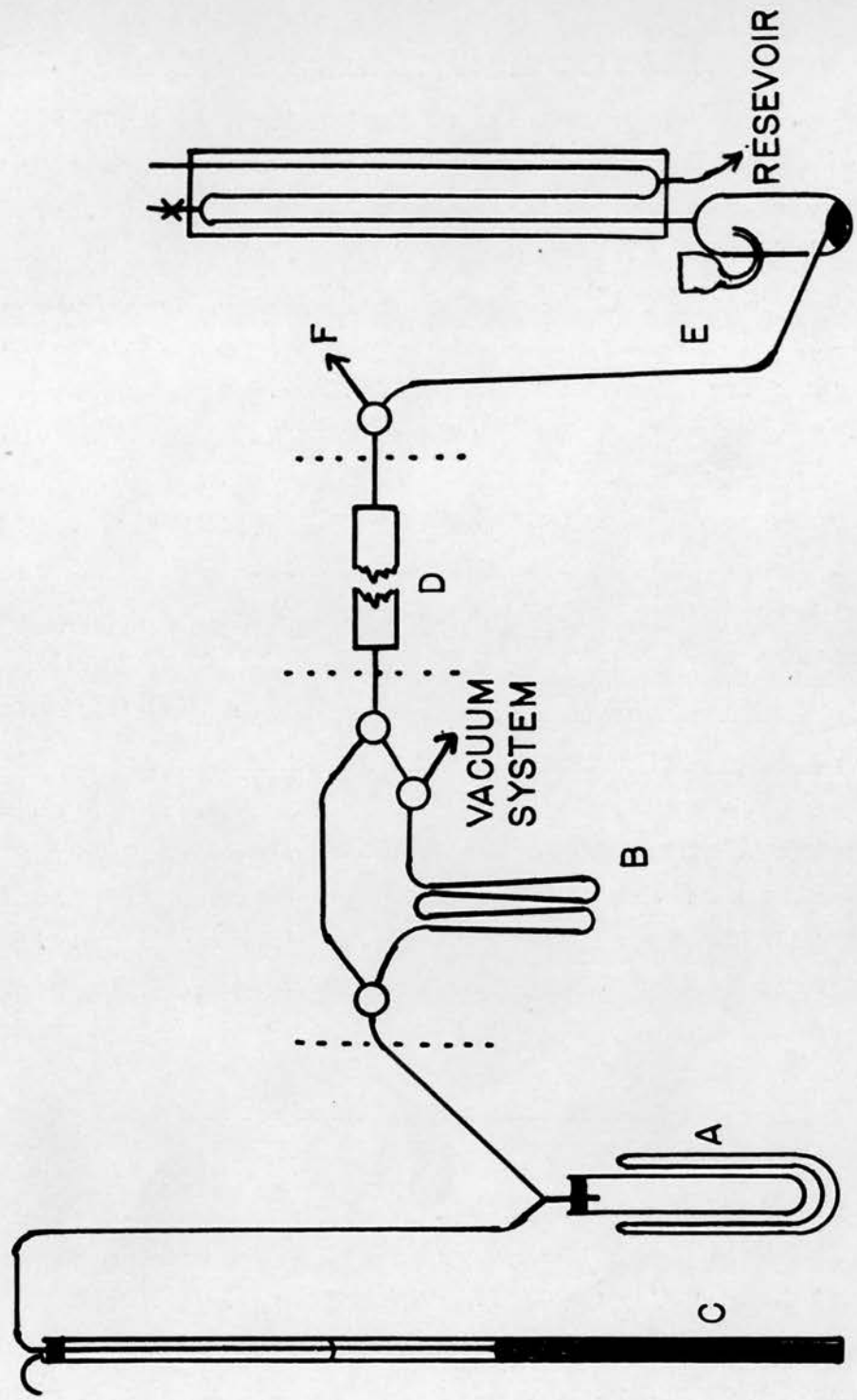
D. Procedure for Alkylperoxy Reactions

The apparatus was evacuated to 10^{-5} mm. The hydrocarbons and ketone were thoroughly degassed. Prior to a series of runs, quantities of two hydrocarbons were accurately measured in the gas burette, and introduced into the mixing vessel to equilibrate. Some ketone was introduced into the preheated reaction vessel, and its pressure measured on the manometer ; some mixture was added, and its pressure measured ; an excess of oxygen was added, and the final pressure was read. The gases were allowed to mix in the reaction vessel, and the lamp to stabilize, for fifteen minutes before the shutter was opened to start the reaction. When the shutter was opened, the temperature of the reaction vessel rapidly rose approximately 5º to the reaction temperature, which was stable to ± 3º for the duration of the reaction.

After a suitable interval the lamp was turned off and the condensable gases were frozen into a W-tube packed with crushed glass helices and immersed in liquid oxygen ; the non-condensable gases were pumped through the sample tube to remove remaining condensables. For mixtures containing methane, the W-tube was packed with activated alumina to condense the methane.

E. Gas Chromatography Apparatus

For analysis a chromatographic system of the Janak design[40] was used (Figure 3), with carbon dioxide as carrier gas. Gaseous carbon monoxide was evolved at a convenient rate from a tube of powdered "Drikold" (A) partly immersed in dry ice/acetone slush. The flow of carrier gas was split, part going to the injection system (B) and part to a mercury bubbler (C) which controlled the pressure head, and therefore the flow rate, of the gas. The injection system consisted of a W-shaped sample tube, which could either be by-passed while connected to the vacuum



ANALYTICAL APPARATUS

FIGURE 3

system, or inserted into the flow. The gas stream next passed into the chromatography columns (D), which are described in detail in the following section. On emerging from the columns, the gas either passed into the detector (E), or was diverted through a flow meter (F) into the atmosphere.

The detector consisted of an absorption vessel (volume ≃ 75 cc) filled with 50 per cent potassium hydroxide solution and connected to a 10 cc gas burette, enlosed in a water jacket. Saturated brine dyed with fluorescein was used in the gas burette, and the liquid level was controlled by a compressible rubber reservoir. Carbon dioxide passing into the detector was absorbed by the potassium hydroxide solution ; non-soluble gases were measured on the gas burette.

To calibrate the detector, standardization runs were carried out at each furnace temperature, using the normal procedure for a reaction and analysis, but omitting all reactants other than the hydrocarbons from the reaction mixture. Factors relating volumes in the Janak detector to hydrocarbon pressures in the reaction vessel were obtained. Systematic errors of calibration were thus eliminated. All volumes were corrected to N.T.P.

Errors due to expansion of the absorbent solution were minimized by making the diameter of the filler tube wide in comparison to the absorption vessel neck, and maintaining the liquid level in the narrow portion of the vessel neck. A small but constant increase in volume, or "drift", (0.01 cc per minute) was observed when carbon dioxide was being absorbed, and appropriate corrections were made to all measurements. The vapour pressures of the burette liquid and the absorbent are negligible at 20º and cause no errors. Changes of flow rate effect only the retention times, and not the quantitative accuracy. The analytical accuracy was about ± 1 %.

Quantities of 0.1 cc (± 0.01 cc) to 10 cc (± 0.05 cc) of C_1 to C_5 hydrocarbons could be estimated in this apparatus ; quantities of 0.02 cc could be detected. Using appropriate

columns, a mixture of two to six hydrocarbons could be analysed in fifteen to sixty minutes.

F. Gas Chromatography Columns

All columns were prepared in 6 mm internal diameter tubing. Oxygenated products which would normally interfere with the hydrocarbon analyses were irreversibly adsorbed by activated alumina, which made up a part of each column system. Olefins were not formed in the alkylperoxy reactions ; consequently, simpler columns were employed to analyse the products of these reactions than could be used for the oxidation products. Flow rates were 30-50 cc/min. Unless otherwise specified, all columns were operated at the ambient temperature. A description of the columns used for the individual mixtures follows.

(i) Mixtures containing olefins

Mixtures of ethane, ethylene, propane or cyclopropane, and propylene were separated on 80 cm of silver nitrate/ethylene glycol/30-40 mesh firebrick[41] followed by 280 cm of 40-60 mesh activated alumina poisoned with 3/4 % squalane.

Ethane, ethylene, methane, and other permanent gases were separated with split columns. The first column consisted of 80 cm of silver nitrate mixture followed by 160 cm of poisoned alumina. The second was 240 cm of Sutcliffe and Speakman 32-40 mesh activated charcoal. During analysis the two columns were at first connected in series, and the methane and other permanent gases eluted onto the charcoal column and isolated. The ethane and ethylene were then eluted from the first column directly into the detector. Finally, the permanent gases were eluted from the charcoal column.

For ethane, ethylene, isobutene, and neopentane a three section column was employed. The first section was 240 cm of 20 % nitrobenzene on 52-72 mesh firebrick ; the second, 80 cm of silver nitrate mixture followed by 160 cm of poisoned alumina ; the third, 120 cm of silver nitrate mixture. In analysis, sections

one and two were first connected in series and carbon dioxide passed until the ethane and ethylene were isolated on the second section of the column. Sections one and three were then connected in series and the isobutene and neopentane eluted directly into the detector. Finally, the ethane and ethylene were eluted from section two.

Isobutene, isobutane, neopentane, and C_2 and C_3 hydrocarbons were separated as follows : the contents of the sample tube were eluted onto a column of 10 cm of poisoned alumina followed by 230 cm of 20 % nitrobenzene on firebrick, and the C_2 and C_3 hydrocarbons were eluted into the atmosphere. The column was then connected in series with 120 cm of silver nitrate mixture, and the C_4 and C_5 hydrocarbons were eluted into the detector.

(ii) Products from alkylperoxy reactions

Cyclopropane, methane, and other permanent gases were separated with split columns. The first column was 120 cm of 40-60 mesh activated alumina poisoned with $1\frac{1}{2}$ % squalane ; the second was 240 cm activated charcoal. The two columns were first connected in series and the methane and other permanent gases eluted onto the charcoal column and isolated. The cyclopropane was then eluted from the first column directly into the detector. Finally, the permanent gases were eluted from the charcoal column.

Carbon monoxide and isobutane were separated with an identical column arrangement at 40°.

All other mixtures were separated on 120 cm of 40-60 mesh activated alumina poisoned with $1\frac{1}{2}$ % squalane. For ethane-propane and ethane-cyclopropane mixtures the column was operated at room temperature ; for propane-isobutane, n-butane-propane, and n-butane-propylene mixtures, at 40-45° ; and for ethane-neopentane and neopentane-propane mixtures, at 65-70°.

3. SPECIMEN EXPERIMENTS

A. Competitive Oxidations

Ethane-neopentane mixture, Run Nº 68

Furnace temperature = 495º
Room temperature = 19º
Induction period = 10 sec
Reaction period = 180 sec
Initial pressure = 299 mm
Final pressure = 345 mm

Composition of reaction mixture

Ethane = 53.45 %
Neopentane = 26.80 %
Oxygen = 19.75 %

∴ Initial concentrations of reactants are :

$$[C_2H_6]_{initial} = 299 \text{ mm} \times 0.5345 = 159.8 \text{ mm}$$

$$[C_5H_{12}]_{initial} = 299 \text{ mm} \times 0.2680 = 80.1 \text{ mm}$$

Factors relating detector volumes to reaction vessel pressures

Ethane ; 1 cc = 20.52 mm
Ethylene ; 1 cc = 20.60 mm
Neopentane ; 1 cc = 20.80 mm
Isobutene ; 1 cc = 20.75 mm

Final concentrations of reactants by analysis

$$[C_2H_6]_{final} = 6.71 \text{ cc} \times 20.52 \text{ mm/cc} = 137.6 \text{ mm}$$

$$[C_5H_{12}]_{final} = 2.66 \text{ cc} \times 20.80 \text{ mm/cc} = 55.3 \text{ mm}$$

Final concentrations of olefin products by analysis

$$[C_2H_4] = 0.93 \text{ cc} \times 20.60 \text{ mm/cc} = 19.2 \text{ mm}$$

$$[\text{iso-}C_4H_8] = 0.56 \text{ cc} \times 20.75 \text{ mm/cc} = 11.6 \text{ mm}$$

Calculation of rate constant ratio

$$\frac{k \text{ (ethane)}}{k \text{ (neopentane)}} = \frac{\log [C_2H_6]_{\text{initial}} - \log [C_2H_6]_{\text{final}}}{\log [C_5H_{12}]_{\text{initial}} - \log [C_5H_{12}]_{\text{final}}}$$

$$= \frac{\log 159.9 - \log 137.6}{\log 80.1 - \log 55.3}$$

$$= \frac{2.2036 - 2.1386}{1.9036 - 1.7427}$$

$$= \frac{0.0650}{0.1609}$$

$$\frac{k \text{ (ethane)}}{k \text{ (neopentane)}} = 0.40$$

B. Competitive Alkylperoxy Radical Reactions

Methylperoxy with ethane-propane mixture ; Run Nº 49

Initial furnace temperature = 227º
Stable reaction temperature = 232º
Total pressure (initial) = 125 mm
Illumination time = 52 min

Composition of hydrocarbon mixture

Ethane = 74.7 %
Propane = 25.3 %

Initial concentrations of reactants

Acetone = 16.1 mm
Oxygen = 77.6 mm

Hydrocarbon mixture = 31.6 mm

$\therefore [C_2H_6]_{initial}$ = 31.6 mm x 0.747 = 23.60 mm

$[C_3H_8]_{initial}$ = 31.6 mm x 0.253 = 8.00 mm

Factors relating detector volumes to reaction vessel pressures

Ethane ; 1 cc = 3.21 mm

Propane ; 1 cc = 3.25 mm

Final concentrations of reactants by analysis

$[C_2H_6]_{final}$ = 6.03 cc x 3.21 mm/cc = 19.35 mm

$[C_3H_8]_{final}$ = 1.52 cc x 3.25 mm/cc = 4.94 mm

Calculation of rate constant ratio

$$\frac{k(\text{ethane})}{k(\text{propane})} = \frac{\log [C_2H_6]_{initial} - \log [C_2H_6]_{final}}{\log [C_3H_8]_{initial} - \log [C_3H_8]_{final}}$$

$$= \frac{\log 23.60 - \log 19.35}{\log 8.00 - \log 4.94}$$

$$= \frac{1.3729 - 1.2867}{0.9031 - 0.6937}$$

$$= \frac{0.0862}{0.2094}$$

$$\frac{k(\text{ethane})}{k(\text{propane})} = 0.41$$

EXPERIMENTAL RESULTS

1. OXIDATION OF ETHANE

The oxidation of methane-ethane mixtures was complicated because methane is an important product of the oxidation of ethane. Therefore, a study of the oxidation of ethane alone at 495° was made to determine the methane yields at different reactant pressures. The results in Table 2 show that with oxygen pressures below about 100 mm, the methane yield was 16 $\pm$ 2 per cent of the ethane consumed in an oxidation. At higher oxygen pressures, the yield of methane was pressure dependent in a mixture of given composition, and fell below 2 per cent at high pressures. The addition of nitrogen had no significant effect.

The experiments showed that ethylene was a major reaction product. The conversion of ethane to ethylene was almost independent of pressure for a given value of $[O_2]/[C_2H_6]$ with the oxygen pressure below 100 mm, but fell at higher oxygen pressures. The variation of the low pressure conversion to ethylene with $[O_2]/[C_2H_6]$ is shown in Figure 4. Extrapolation to zero $[O_2]/[C_2H_6]$ shows that in oxygen weak mixtures about 80 per cent of the ethane removed is converted to ethylene. This figure agrees with that obtained by Knox and Wells[42] for the initial conversion of ethane to ethylene at 360°. It is also in general agreement with the known yields of olefins obtained in other high temperature oxidations (eg. of propane ; Satterfield and Wilson[10], Falconer and Knox[9]). When the oxygen pressure exceeded 100 mm, the conversion to ethylene fell sharply with pressure. The ethylene yield was low when the amount of residual methane was also low.

2. COMPETITIVE OXIDATIONS

The rate constant ratios for mixed oxidations of the following pairs of saturated hydrocarbons have been calculated from the equation

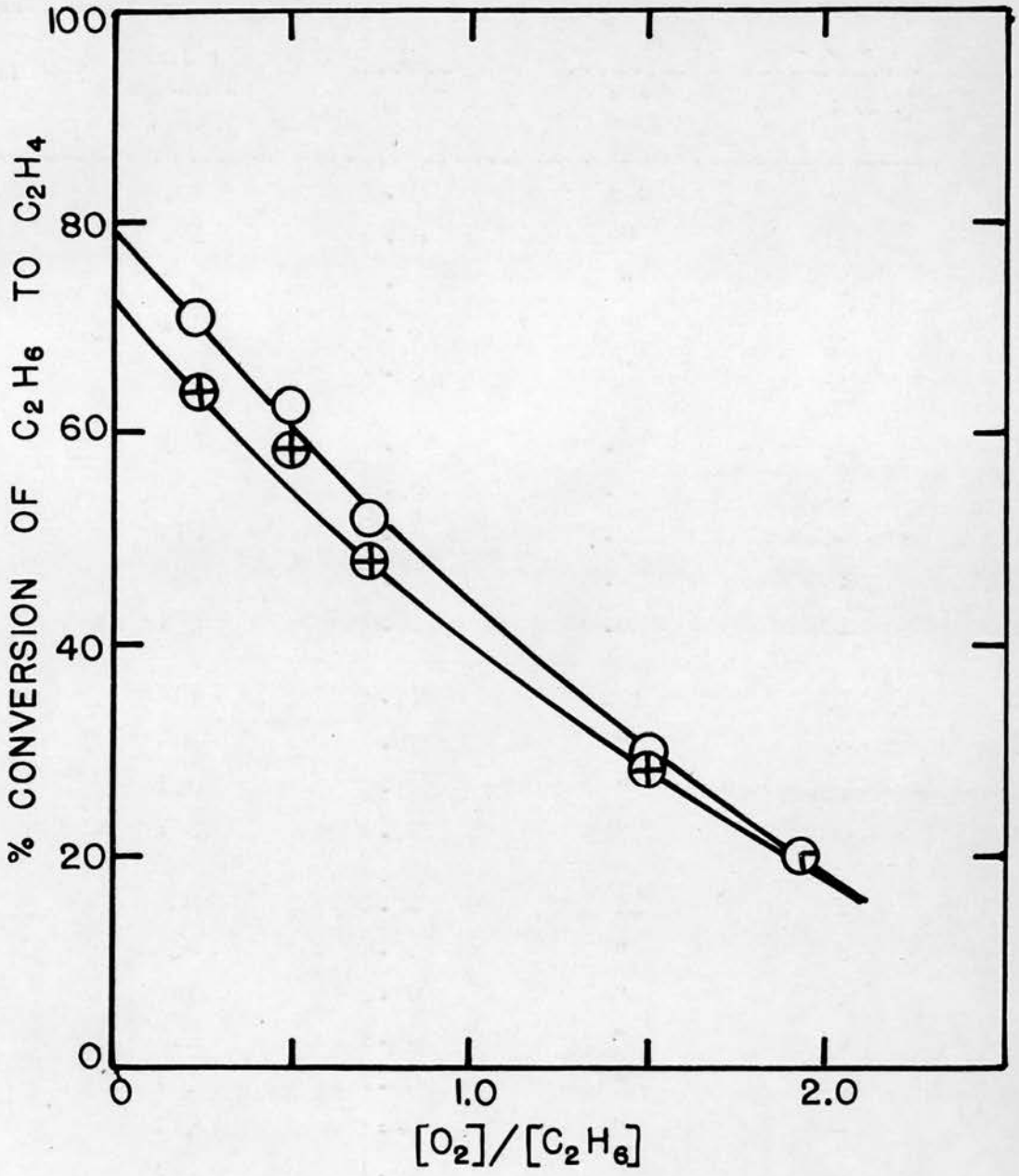
Table 2

OXIDATION OF ETHANE AT 495°

Run N°	Total Pressure (mm)	$\frac{[O_2]}{[C_2H_6]}$	$\frac{[N_2]}{\text{Total Pressure}}$	$\frac{100\ C_2H_4}{C_2H_6\text{(cons.)}^{**}}$	$\frac{100\ CH_4}{C_2H_6\text{(cons.)}^{**}}$
1	362	0.25	nil	60	13.8
2	291	0.25	"	62	15.1
3	196	0.25	"	65	19.4
4	104	0.25	"	75	16.0
5	102	0.25	"	58	13.3
19	403	0.48	0.32	58	16.7
20	304	0.48	0.32	57	15.8
18	214	0.48	0.32	56	13.0
22	202	0.48	0.32	61	14.1
21	109	0.48	0.32	61	18.4
10	217	0.72	nil	46	20.7
6	200	0.72	"	46	15.2
8	154	0.72	"	49	16.3
9	104	0.72	"	50	16.8
14	288	1.50	nil	1	1.5*
13	250	1.50	"	1	1.7*
12	201	1.50	"	3	6.6*
15	179	1.50	"	13	7.5*
16	165	1.50	"	26	15.2
11	149	1.50	"	-	15.4
17	108	1.50	"	28	15.6
23	355	1.93	0.33	1	0.4*
24	272	1.93	0.33	0	1.9*
25	204	1.93	0.33	20	11.3
26	153	1.93	0.33	20	13.2
27	96	1.93	0.33	20	15.0

(*) These values are not included in the average value used as a correction factor in calculating k(methane)/k(ethane).

(**) C_2H_6 (cons.) is the amount of ethane consumed during a run.



DEPENDENCE OF THE CONVERSION OF ETHANE TO ETHYLENE UPON $[O_2]/[C_2H_6]$ AT 495°

⊕, $[O_2]$ = 100 MM ; O, $[O_2]$ = 0.

FIGURE 4

$$\frac{k_a}{k_b} = \frac{\log [R_aH]_{initial} - \log [R_aH]_{final}}{\log [R_bH]_{initial} - \log [R_bH]_{final}} .$$

A. Methane-ethane Mixtures

The oxidation of methane-ethane mixtures was studied only at 495° since the rate of oxidation at lower temperatures was very low at accessible pressures. In some experiments, the oxidation of ethane yielded so much methane that the methane content of the mixture increased. In order to minimize the effect of the methane thus formed, all mixtures studied contained at least as much methane as ethane. Experiments were carried out only under conditions where a 16 per cent yield of methane from ethane was to be expected. An appropriate correction to the methane concentration was made in calculating k(methane)/k(ethane). The reproducibility of this ratio at constant oxygen concentration when $[CH_4]/[C_2H_6]$ varies between 4:1 and 1:1 is evidence for the validity of the applied correction.

The results in Table 3 show that the relative rates of consumption of methane and ethane under these conditions are independent of the total pressure for a mixture of given composition, but are strongly dependent upon $[O_2]/[RH]$. Extrapolation of a plot of k(methane)/k(ethane) against $[O_2]/[RH]$ (Figure 5) to zero oxygen concentration gives a value of k(methane)/k(ethane) = 0.04.

B. Cyclopropane-ethane Mixtures

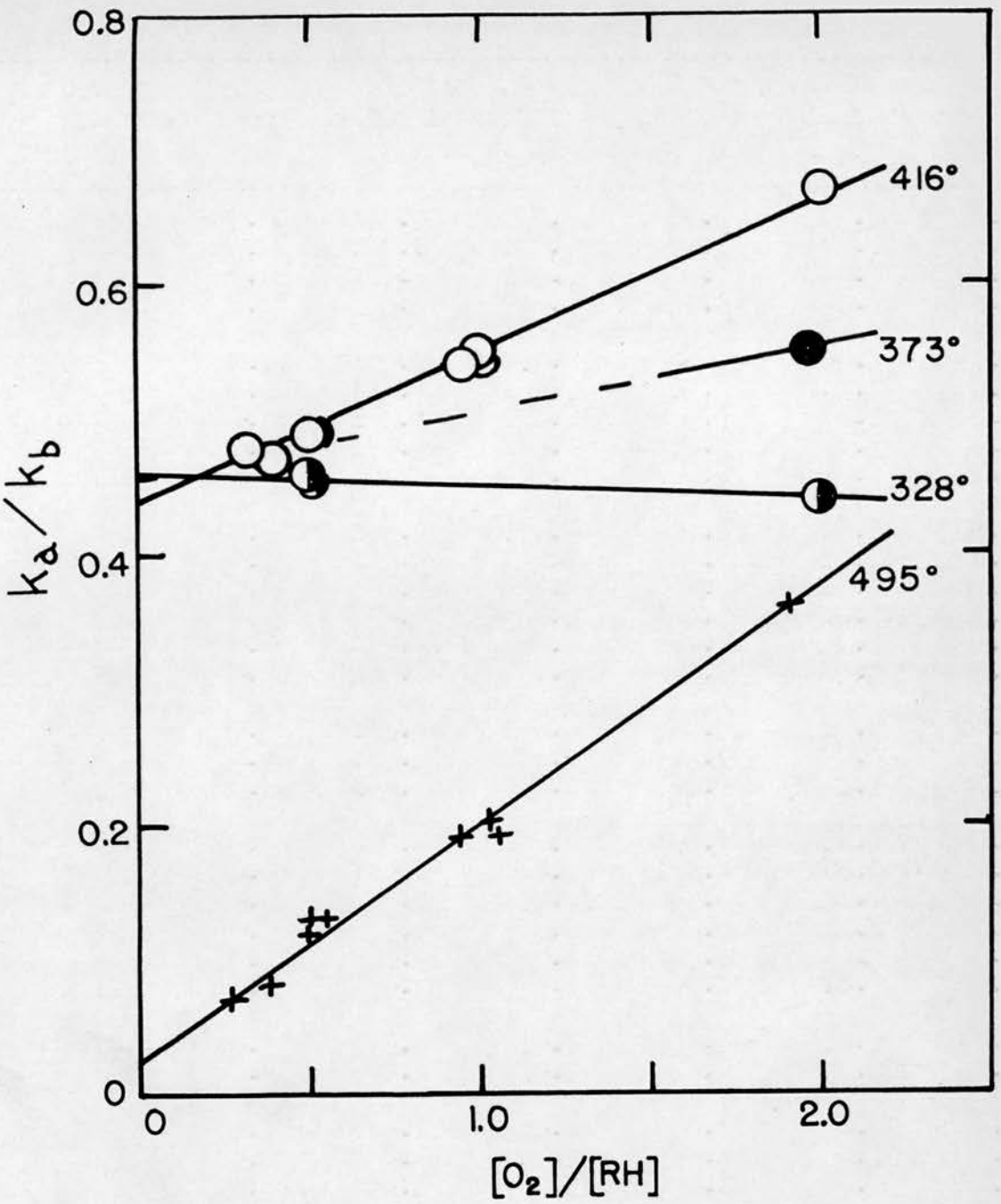
The oxidation of this mixture is complicated by the possible isomerization of cyclopropane to propylene at higher temperatures. Below 416°, less than 1 per cent of the cyclopropane isomerized during a run and an appropriate correction was made to the cyclopropane concentration when calculating k(cyclopropane)/k(ethane). The addition of 1-5 per cent acetaldehyde to some of the reaction mixtures at 328° and 373° to reduce the otherwise long induction periods did not affect the relative rates of consumption.

Table 3

OXIDATION OF METHANE-ETHANE MIXTURES AT 495°

Run N°	Total Pressure (mm)	$\frac{[O_2]}{[RH]}$	[Methane] initial (mm)	[Methane] final (mm) *	[Ethane] initial (mm)	[Ethane] final (mm)	$\frac{k(methane)}{k(ethane)}$
38	363	0.26	190.7	181.8	97.8	48.2	0.07
39	282	0.26	148.1	140.6	76.0	34.4	0.06
37	244	0.26	127.9	119.5	65.7	29.2	0.08
40	182	0.26	98.5	94.5	50.5	21.9	0.04
42	353	0.38	169.5	151.2	86.0	29.9	0.10
43	297	0.38	142.8	132.4	72.3	28.1	0.08
45	256	0.38	123.2	113.0	62.4	21.3	0.08
41	248	0.38	117.2	106.6	59.4	20.7	0.09
44	211	0.38	101.6	94.5	51.5	16.8	0.07
11	352	0.49	158.3	137.9	77.3	24.7	0.12
12	296	0.49	133.2	113.9	65.1	19.1	0.13
13	279	0.49	125.5	106.4	61.4	17.6	0.13
14	206	0.49	92.8	81.7	45.3	11.0	0.09
15	154	0.49	69.3	59.3	33.9	8.0	0.11
16	111	0.49	50.0	41.5	24.4	5.2	0.12
35	339	0.50	181.0	147.8	44.7	10.8	0.14
36	296	0.50	158.0	130.5	39.1	9.0	0.13
34	255	0.50	136.4	112.1	33.7	7.4	0.13
28	422	0.55	132.8	108.9	140.0	23.9	0.11
29	375	0.55	118.2	100.0	124.5	27.1	0.11
30	286	0.55	90.1	76.4	94.8	30.5	0.15
31	213	0.55	67.1	57.8	70.7	22.2	0.14
27	204	0.55	64.2	53.2	67.7	20.6	0.16
32	133	0.55	41.9	36.4	44.2	11.3	0.11
3	327	0.96	110.2	78.5	55.3	10.5	0.20
4	187	0.96	62.9	43.3	31.6	3.9	0.18
53	318	1.03	124.7	82.1	32.3	4.3	0.21
52	249	1.03	97.6	63.5	25.3	2.4	0.18
54	237	1.03	92.8	60.4	24.1	2.8	0.20
49	290	1.05	92.2	64.0	49.3	7.5	0.19
46	259	1.05	82.3	55.1	44.1	5.8	0.20
50	202	1.05	64.2	44.6	34.3	4.9	0.19
51	153	1.05	48.7	32.5	26.0	2.4	0.17
55	303	1.90	69.4	31.0	34.8	3.7	0.36
56	274	1.90	62.7	24.8	31.4	2.8	0.38
57	203	1.90	46.4	20.4	23.3	1.9	0.33

* The values listed for $[Methane]_{final}$ have been corrected for methane produced from ethane.



DEPENDENCE OF THE RELATIVE RATES OF OXIDATION ON $[O_2]/[RH]$

O, a = CYCLOPROPANE ; b = ETHANE

+, a = METHANE ; b = ETHANE

FIGURE 5

The results tabulated in Table 4 show that the relative rates of consumption of cyclopropane and ethane are independent of total pressure, and of the cyclopropane to ethane ratio between 1:3 and 3:1. Figure 5 shows that k(cyclopropane)/k(ethane) is independent of $[O_2]/[RH]$ at 328°, but increases markedly with $[O_2]/[RH]$ at the higher temperatures studied. The value of k(cyclopropane)/k(ethane) at zero $[O_2]/[RH]$ is temperature independent at 0.45 between 328° and 416°.

Ethylene was a major reaction product. The ethylene conversions for $[O_2]/[RH] = 0$ rose from about 60 per cent of the ethane consumed at 328° to nearly 100 per cent at 416°.

C. Ethane-neopentane Mixtures

Neopentane is a particularly interesting hydrocarbon from the point of view of oxidation since no pentene can be formed from it without a molecular rearrangement. The oxidation of neopentane might therefore involve radicals different from those taking part in the oxidations of other hydrocarbons, and there might be a strong dependence of the relative rates of removal on the neopentane to ethane ratio. The results in Table 5 show that this is not the case. The relative rate constants are independent of this ratio over a sixfold range, and are also independent of the total pressure for mixtures of a given composition. Figure 6B shows that the rate of removal of ethane relative to neopentane is independent of $[O_2]/[RH]$ at the lowest temperature (328°) but increases with $[O_2]/[RH]$ at higher temperatures. Whereas in the oxidations of methane-ethane and cyclopropane-ethane mixtures the ethane becomes relatively less reactive as $[O_2]/[RH]$ is increased, it becomes relatively more reactive in ethane-neopentane mixtures. In Figure 7, the logarithms of the rate constant ratios extrapolated to zero $[O_2]/[RH]$ are plotted against the reciprocal absolute temperature. The relative rates of removal of hydrocarbons between 328-495° at $[O_2]/[RH] = 0$ are given by :

$$\frac{k(\text{ethane})}{k(\text{neopentane})} = 0.14 \exp(1600/RT).$$

Table 4

OXIDATION OF CYCLOPROPANE-ETHANE MIXTURES

Run N°	Total Pressure (mm)	$\frac{[O_2]}{[RH]}$	[Cyclopropane] initial (mm)	[Cyclopropane] final (mm)	[Ethane] initial (mm)	[Ethane] final (mm)	$\frac{k(\text{cyclopropane})}{k(\text{ethane})}$
TEMPERATURE = 328°							
87	390	0.49	174.4	149.4	86.2	59.7	0.45
88	300	0.49	133.8	114.3	66.2	47.5	0.47
90	202	0.49	90.4	82.0	44.7	36.1	0.46
104	360	0.50	79.6	69.9	165.0	122.6	0.44
106	250	0.50	55.5	49.3	115.0	87.4	0.45
97	230	0.50	50.6	45.8	101.4	79.8	0.42
93	164	0.50	36.3	32.3	72.8	56.0	0.45
98	164	0.50	36.1	30.9	72.2	53.2	0.49
102	147	0.50	31.8	28.3	65.8	50.3	0.43
94	119	0.50	26.3	23.2	52.8	40.2	0.46
103	104	0.50	22.4	19.8	46.6	34.9	0.43
107	442	2.00	72.2	45.0	71.2	22.7	0.41
112	401	2.00	68.0	56.1	67.3	44.0	0.45
113	320	2.00	54.4	36.7	53.8	21.2	0.43
108	311	2.00	50.8	41.6	50.1	30.7	0.41
114	231	2.00	39.2	30.1	38.7	21.2	0.44
109	220	2.00	36.0	29.9	35.5	23.8	0.47
115	162	2.00	27.5	23.3	27.2	18.9	0.45
110	156	2.00	25.5	20.5	25.1	15.5	0.45
111	110	2.00	18.0	12.7	17.7	8.6	0.47
TEMPERATURE = 373°							
122	245	1.96	54.8	48.3	27.4	21.8	0.55
119	180	1.96	40.7	29.4	19.6	10.8	0.55
123	176	1.96	39.4	17.5	19.7	4.2	0.53
TEMPERATURE = 416°							
49	355	0.33	66.4	58.4	199.1	146.0	0.49
50	294	0.33	55.2	47.6	164.5	118.2	0.52
51	169	0.33	31.8	27.4	94.7	65.9	0.46
52	98	0.33	18.3	15.6	54.7	36.4	0.43
35	293	0.35	161.0	139.2	55.1	40.0	0.46
36	226	0.35	124.0	105.2	42.3	30.5	0.50
37	155	0.35	85.2	71.8	29.1	19.8	0.44
38	142	0.35	78.2	63.8	26.8	17.7	0.48
39	85	0.35	46.7	39.6	15.9	10.6	0.47

Table 4 (continued)

OXIDATION OF CYCLOPROPANE-ETHANE MIXTURES

Run N°	Total Pressure (mm)	$\frac{[O_2]}{[RH]}$	[Cyclopropane] initial (mm)	[Cyclopropane] final (mm)	[Ethane] initial (mm)	[Ethane] final (mm)	$\frac{k(\text{cyclopropane})}{k(\text{ethane})}$
TEMPERATURE = 416°							
32	403	0.50	198.2	166.5	66.6	46.6	0.46
27	297	0.50	147.8	119.0	50.6	31.4	0.46
33	257	0.50	126.4	100.0	42.3	26.4	0.50
28	224	0.50	111.1	88.1	38.0	23.3	0.51
29	154	0.50	76.6	59.7	26.2	15.2	0.46
34	148	0.50	73.1	55.6	24.4	14.7	0.54
30	101	0.50	50.0	37.3	17.1	9.5	0.50
31	79	0.50	39.2	29.2	13.4	7.6	0.52
57	405	0.51	67.2	54.0	200.6	123.0	0.50
58	311	0.51	51.6	41.6	153.8	91.3	0.46
59	198	0.51	32.8	25.1	97.8	53.8	0.48
60	114	0.51	18.8	10.0	56.2	19.1	0.52
64	325	0.95	81.3	51.5	84.8	36.3	0.54
65	188	0.95	46.8	28.7	48.9	18.6	0.53
40	430	1.00	160.6	105.5	53.3	25.0	0.55
41	326	1.00	121.7	79.2	40.4	18.6	0.55
42	246	1.00	91.8	55.0	30.5	12.3	0.56
43	156	1.00	58.2	35.8	19.3	7.5	0.52
44	89	1.00	33.3	19.9	11.0	4.1	0.52
53	437	1.00	53.2	34.8	164.1	72.9	0.54
45	420	1.00	53.2	33.1	157.8	67.3	0.59
46	266	1.00	33.7	21.4	98.8	37.3	0.52
54	256	1.00	31.4	19.6	96.5	37.0	0.54
47	151	1.00	19.2	12.4	56.8	20.1	0.52
55	148	1.00	17.8	10.1	54.7	18.7	0.55
56	85	1.00	10.3	5.6	31.8	9.6	0.56
74	456	2.00	75.6	26.9	76.8	16.7	0.68
79	413	2.00	68.7	24.0	67.3	14.1	0.67
76	370	2.00	59.6	17.5	62.6	10.2	0.68
80	300	2.00	50.1	15.8	49.0	8.3	0.65
77	271	2.00	43.7	12.4	45.8	6.7	0.66
75	260	2.00	43.2	10.9	43.8	6.0	0.69

Table 5

OXIDATION OF ETHANE-NEOPENTANE MIXTURES

Run N°	Total Pressure (mm)	$\frac{[O_2]}{[RH]}$	[Ethane] initial (mm)	[Ethane] final (mm)	[Neopentane] initial (mm)	[Neopentane] final (mm)	$\frac{k(\text{ethane})}{k(\text{neopentane})}$
TEMPERATURE = 328°							
92	320	0.33	123.8	107.8	118.3	91.4	0.53
88	311	0.33	117.8	101.8	117.2	89.9	0.53
89	234	0.33	88.8	76.4	88.4	65.8	0.52
49	327	0.64	131.1	102.2	68.0	41.0	0.49
50	255	0.64	102.3	78.5	53.0	31.3	0.51
87	242	0.64	97.6	71.5	49.3	27.3	0.52
51	179	0.64	71.8	55.0	37.2	21.8	0.50
55	389	1.50	103.4	62.4	50.2	19.3	0.53
56	294	1.50	78.2	41.0	37.9	11.8	0.55
90	282	1.50	76.3	46.0	39.3	15.0	0.52
91	250	1.50	67.5	39.2	34.9	13.5	0.56
57	245	1.50	65.2	36.9	31.6	11.0	0.56
58	406	2.96	69.4	40.8	33.4	12.1	0.53
59	367	2.96	62.7	33.1	30.2	9.3	0.54
60	271	2.96	46.4	24.6	22.3	6.8	0.54
TEMPERATURE = 421°							
20	330	0.25	175.3	154.2	86.9	65.6	0.46
79	270	0.25	141.8	120.0	72.0	51.9	0.50
19	258	0.25	137.0	119.2	68.0	49.8	0.45
22	255	0.25	135.5	118.4	67.3	50.8	0.48
21	181	0.25	96.3	82.6	47.8	34.9	0.49
23	323	0.25	85.8	77.4	171.9	136.2	0.45
26	278	0.25	73.9	67.0	148.3	121.9	0.49
24	249	0.25	66.2	58.6	132.6	104.1	0.50
25	206	0.25	54.8	49.3	109.8	87.6	0.46
1	303	0.50	103.5	80.2	97.2	57.7	0.49
77	266	0.50	88.5	67.8	88.7	52.9	0.51
2	254	0.50	86.8	69.3	81.5	49.8	0.46
5	254	0.50	86.7	69.7	81.4	52.3	0.49
3	202	0.50	69.1	55.4	64.8	40.4	0.47
6	162	0.50	55.5	44.2	52.1	32.5	0.48
12	404	0.50	202.0	152.2	68.0	37.8	0.48
8	390	0.50	193.8	145.0	67.1	39.5	0.54
13	302	0.50	151.2	111.8	50.8	27.2	0.49
7	301	0.50	149.2	110.2	51.7	28.5	0.51
9	256	0.50	127.0	95.2	44.0	24.2	0.48
14	199	0.50	99.6	72.2	33.5	17.5	0.49
11	173	0.50	86.2	77.4	29.7	23.4	0.46

Table 5 (continued)

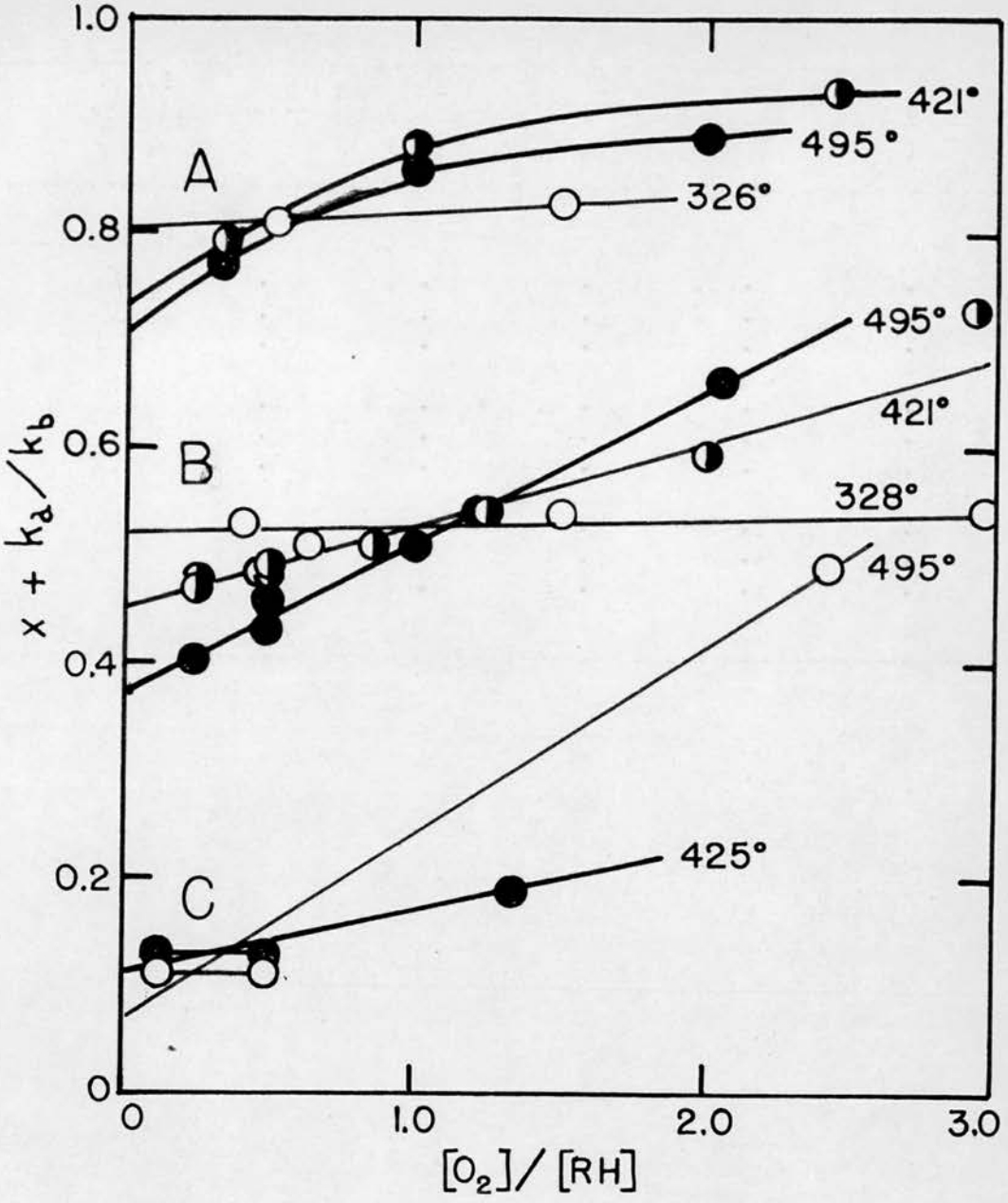
OXIDATION OF ETHANE-NEOPENTANE MIXTURES

Run N°	Total Pressure (mm)	$\frac{[O_2]}{[RH]}$	[Ethane] initial (mm)	[Ethane] final (mm)	[Neopentane] initial (mm)	[Neopentane] final (mm)	$\frac{k(\text{ethane})}{k(\text{neopentane})}$
TEMPERATURE = 421°							
15	378	0.50	86.7	69.4	166.4	101.9	0.46
78	305	0.50	67.9	52.2	140.1	84.8	0.51
16	258	0.50	59.0	47.7	113.2	73.8	0.50
17	203	0.50	46.5	37.8	89.2	57.2	0.47
18	127	0.50	29.1	23.9	55.8	36.8	0.48
27	402	0.82	149.2	99.8	73.8	31.3	0.48
29	353	0.82	126.9	83.2	65.3	29.5	0.53
31	297	0.82	106.8	70.2	54.9	25.0	0.53
30	258	0.82	92.8	60.4	47.7	20.3	0.51
32	200	0.82	71.8	48.7	36.9	16.0	0.50
33	424	1.22	127.6	71.0	64.0	20.5	0.52
34	356	1.22	107.0	57.4	53.7	16.4	0.53
35	278	1.22	83.5	44.8	41.9	13.4	0.55
81	272	1.22	84.4	46.3	39.9	13.6	0.56
36	187	1.22	56.1	28.9	28.2	8.5	0.55
38	309	1.26	45.4	27.6	90.6	34.8	0.52
39	257	1.26	38.7	22.1	77.4	26.7	0.53
83	208	1.26	31.6	19.2	62.4	25.9	0.56
40	188	1.26	28.3	16.3	56.7	20.4	0.54
42	339	2.00	75.6	26.3	37.8	6.2	0.59
84	289	2.00	60.6	22.9	32.2	6.0	0.58
43	246	2.00	54.8	18.8	27.4	4.4	0.59
44	179	2.00	40.0	12.7	20.0	2.8	0.59
45	382	2.92	63.9	11.2	33.3	3.4	0.77
47	341	2.92	57.2	9.9	29.7	2.7	0.73
46	338	2.92	56.6	9.9	29.5	2.6	0.72
85	309	2.92	50.7	8.7	27.5	3.6	0.73
48	254	2.92	42.5	6.5	22.2	1.7	0.73
TEMPERATURE = 495°							
67	371	0.25	198.4	169.2	99.3	67.9	0.42
68	299	0.25	159.8	137.6	80.1	55.3	0.40
69	212	0.25	113.3	100.6	56.7	40.7	0.37
66	363	0.50	161.9	122.4	79.5	41.6	0.43
64	294	0.50	131.0	99.2	63.4	32.0	0.41
65	227	0.50	101.3	75.2	49.8	25.4	0.44

Table 5 (continued)

OXIDATION OF ETHANE-NEOPENTANE MIXTURES

Run N°	Total Pressure (mm)	$\frac{[O_2]}{[RH]}$	[Ethane] initial (mm)	[Ethane] final (mm)	[Neopentane] initial (mm)	[Neopentane] final (mm)	$\frac{k(\text{ethane})}{k(\text{neopentane})}$
TEMPERATURE = 495°							
61	314	0.50	70.6	50.7	139.0	68.0	0.46
63	246	0.50	55.3	42.5	109.0	58.2	0.42
62	162	0.50	36.5	27.1	71.7	38.9	0.49
70	290	1.00	95.9	52.8	48.3	16.0	0.54
71	277	1.00	91.6	51.9	46.2	13.9	0.48
72	177	1.00	58.6	33.1	29.5	9.4	0.50
73	290	2.06	64.1	17.3	30.7	4.4	0.68
74	265	2.06	58.6	15.4	28.1	3.6	0.66
75	224	2.06	49.5	12.5	23.7	2.5	0.61



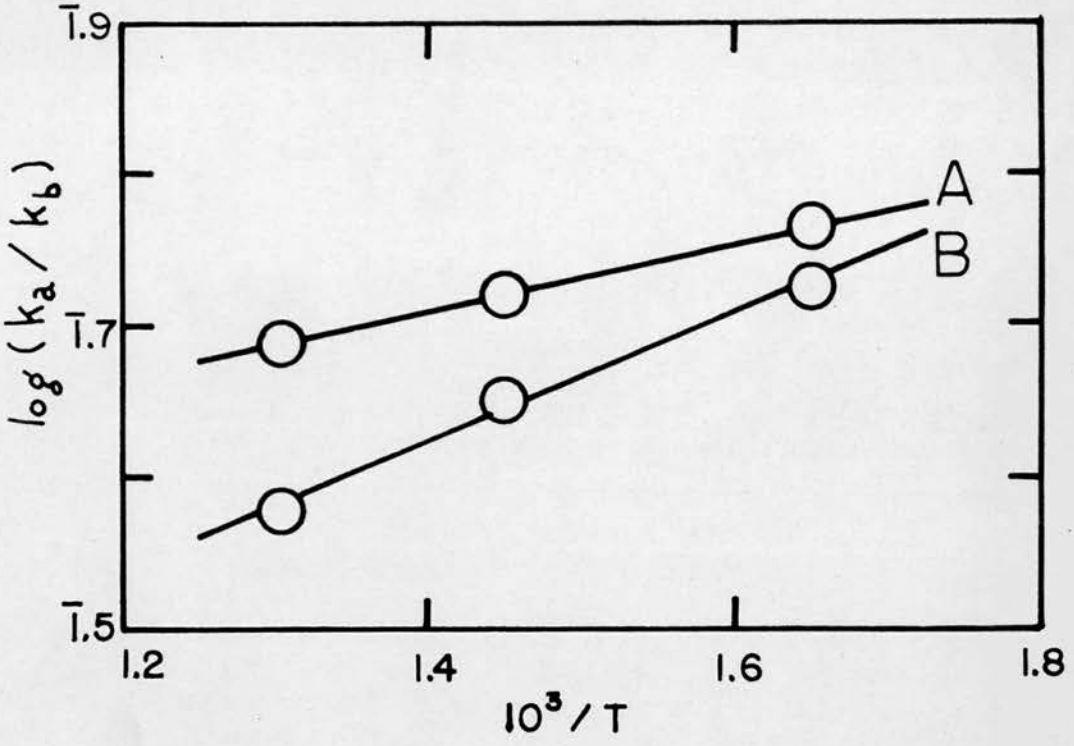
DEPENDENCE OF THE RELATIVE RATES OF OXIDATION ON $[O_2]/[RH]$

A, a = NEOPENTANE ; b = ISOBUTANE ; X = 0.2

B, a = ETHANE ; b = NEOPENTANE ; X = 0

C, a = ETHANE ; b = PROPANE ; X = ~0.3

FIGURE 6



TEMPERATURE VARIATION OF RELATIVE RATE CONSTANTS IN COMPETITIVE OXIDATIONS WHEN $[O_2]/[RH]=0$

A, a = NEOPENTANE ; b = ISOBUTANE

B, a = ETHANE ; b = NEOPENTANE

FIGURE 7

A brief study of the oxidation of neopentane alone at 495° showed that although no pentene was formed, isobutene was a major reaction product. It is presumably formed by the pyrolysis of the neopentyl radical,

$$Me_3CCH_2\cdot \longrightarrow Me_2C{=}CH_2 + Me\cdot .$$

In the competitive oxidations, the proportion of neopentane converted to isobutene increased with temperature, probably because the decomposition of the neopentyl radical has a higher activation energy than its oxidation.

D. Neopentane-isobutane Mixtures

Only 1:1 neopentane-isobutane mixtures were investigated. Table 6 shows the relative rates of consumption to be independent of total pressure for mixtures of given $[O_2]/[RH]$. At 326° there was no dependence upon $[O_2]/[RH]$, but, as Figure 6A shows, at higher temperatures the neopentane became relatively more reactive as $[O_2]/[RH]$ was increased. A plot of the logarithms of the rate constant ratios at $[O_2]/[RH] = 0$ against reciprocal temperature, Figure 7, gives for the temperature range 326-495° :

$$\frac{k(\text{neopentane})}{k(\text{isobutane})} = 0.26 \exp(1000/RT).$$

Isobutene is a major product of the oxidation of both isobutane and neopentane.

The oxygen dependence for this and the previous mixture indicates that there should be a strong oxygen dependence in the ethane-isobutane oxidation.

E. Ethane-propane Mixtures

The ethane-propane system was extensively studied by Knox, Smith, and Trotman-Dickenson[13] with mixtures in which $[O_2]/[RH]$ was less than 0.50 . In this region, no dependence of k(ethane)/k(propane) upon total pressure, relative hydrocarbon concentration, or oxygen to hydrocarbon ratio was observed.

Table 6

OXIDATION OF NEOPENTANE-ISOBUTANE MIXTURES

Run N°	Total Pressure (mm)	$\frac{[O_2]}{[RH]}$	[Neopentane] initial (mm)	[Neopentane] final (mm)	[Isobutane] initial (mm)	[Isobutane] final (mm)	$\frac{k(\text{neopentane})}{k(\text{isobutane})}$
TEMPERATURE = 326°							
1	367	0.52	122.4	98.2	120.1	82.3	0.59
2	256	0.52	84.8	66.8	84.1	57.7	0.62
3	297	1.50	59.8	34.2	59.8	24.6	0.63
4	235	1.50	47.3	27.3	47.3	19.8	0.63
TEMPERATURE = 421°							
5	331	0.35	121.6	95.9	122.6	81.4	0.58
6	195	0.35	71.6	57.3	72.2	49.5	0.59
7	344	1.00	85.5	46.7	85.5	34.7	0.67
8	277	1.00	68.8	37.8	68.8	28.6	0.68
10	283	2.45	42.0	12.5	41.6	8.1	0.74
9	271	2.45	40.2	12.5	39.8	7.8	0.72
TEMPERATURE = 492°							
12	297	0.33	111.0	78.5	112.8	62.6	0.59
11	267	0.33	99.8	70.0	101.4	53.7	0.56
14	180	1.00	45.5	22.5	45.5	16.7	0.65
13	161	1.00	40.6	20.6	40.6	14.6	0.66
15	178	2.00	29.7	10.5	29.4	6.4	0.68
16	164	2.00	27.4	8.7	27.1	5.3	0.70

A few experiments with higher $[O_2]/[RH]$, included in Table 7, showed that ethane appears more reactive as $[O_2]/[RH]$ is increased at 425° and 495°. A comparison of Figures 6B and 6C shows that the $[O_2]/[RH]$ dependence for ethane-propane mixtures is similar to that of the ethane-neopentane system. Consequently, the relative oxidation rates of propane and neopentane should be nearly independent of $[O_2]/[RH]$.

F. Effect of Additives to Ethane-propane Mixtures

In the five systems studied it was observed that the relative rates of oxidation were dependent upon $[O_2]/[RH]$, except at the lowest temperatures ($\sim$328°), and that the effect of changes in this ratio increased with temperature (see Figures 5 and 6). These results indicate that the reaction products play an important part in governing the composition of the free radical mixture which removes the parent hydrocarbons in the later stages of oxidation at higher temperatures. Therefore experiments were carried out with some of the more probable initial products added to ethane-propane mixtures, in an attempt to induce the high oxygen concentration behavior in oxygen weak mixtures.

The results presented in Table 7 show that additions of ethylene, propylene, methanol, or formic acid have no significant effect at 425°. Hydrogen and formic acid likewise were ineffective at 495°. Acetaldehyde, normally regarded as a potent accelerator of oxidations, had only a slight effect at 495° and no effect at 425°. At 495°, 10 per cent was required to give a moderate increase in k(ethane)/k(propane). This amount is far in excess of that likely to be present in the oxidations, and its effect is considerably less than that obtained by adding more oxygen. The effect was not enhanced by adding olefins and acetaldehyde simultaneously.

These experiments were, unfortunately, unable to provide direct evidence as to the cause of the marked dependence of the relative rates of oxidation on the oxygen to hydrocarbon

Table 7

EFFECT OF ADDITIVES ON ETHANE-PROPANE OXIDATION AT

Run N°	Additive	$\frac{[O_2]}{[RH]}$	[Ethane] initial (mm)	[Ethane] final (mm)	[Propane] initial (mm)	[Propane] final (mm)	$\frac{k(\text{ethane})}{k(\text{propane})}$
TEMPERATURE = 425°							
-	none	0.50	-	-	-	-	0.43[13]
1	40 % C_2H_4	0.25	61.6	50.6	60.4	39.8	0.48
2	"	0.25	51.3	43.5	50.3	34.3	0.43
3	"	0.25	38.0	32.1	37.3	25.2	0.43
4	50 % C_2H_4	0.25	59.5	53.1	57.4	45.1	0.44
5	"	0.25	37.0	33.9	35.7	28.9	0.42
13	17 % CH_3OH	0.47	91.1	70.0	93.6	48.3	0.40
14	"	0.47	66.8	50.5	68.7	33.9	0.40
15	"	0.47	49.1	37.4	50.4	26.4	0.42
10	23 % C_3H_6	0.50	86.3	72.9	85.6	55.8	0.40
11	"	0.50	67.7	55.3	67.1	43.6	0.47
12	"	0.50	50.1	42.3	49.7	33.5	0.43
16	6 % HCOOH	0.57	94.6	65.1	91.6	39.1	0.44
17	"	0.57	85.2	58.3	82.6	35.1	0.45
18	"	0.57	64.3	43.7	62.2	26.5	0.45
8	none	1.35	67.2	32.1	74.2	16.5	0.49
9	"	1.35	54.4	26.4	60.0	13.5	0.49
6	23 % C_2H_4	1.35	39.2	25.7	38.8	17.0	0.51
7	"	1.35	28.7	17.7	28.4	11.0	0.51
TEMPERATURE = 495°							
-	none	0.50	-	-	-	-	0.41[13]
26	"	0.34	88.3	66.4	89.3	44.3	0.41
35	2 % CH_3CHO	0.34	93.6	68.7	93.3	46.3	0.44
34	"	0.34	74.5	54.2	74.3	36.6	0.45
33	25 % CH_3CHO	0.33	57.2	35.8	56.1	23.1	0.53
32	"	0.33	54.7	35.3	53.6	23.3	0.53
19	19 % H_2	0.34	97.0	63.0	96.2	36.2	0.44
20	"	0.34	72.3	48.2	71.7	29.3	0.45
21	6 % HCOOH	0.42	115.5	75.2	117.6	41.7	0.42
30	10 % CH_3CHO	0.41	58.6	39.5	53.9	24.7	0.51
31	+ 10 % C_3H_6	0.41	52.8	36.3	48.6	23.1	0.51
24	10 % CH_3CHO	0.42	64.5	41.3	64.5	28.0	0.53
25	+ 10 % C_2H_4	0.42	62.3	40.4	62.3	26.6	0.51
22	11 % CH_3CHO	0.50	60.8	36.4	61.2	22.9	0.52
23	"	0.50	54.9	34.7	55.3	23.8	0.55
29	none	2.45	28.2	4.8	28.2	2.7	0.76
28	"	2.45	27.7	3.8	27.7	2.4	0.81

ratio. The effect is not caused by the oxidation of any of the products listed in Table 7.

3. OXIDATIONS OF OLEFINS

During the study of the addition of ethylene to ethane-propane mixtures, the ethane consumption was sometimes found to be unexpectedly small. Ethylene was therefore oxidized separately, and ethane was obtained in considerable quantity (up to 11 per cent) as a product if the reaction was allowed to proceed to completion. If, however, the reaction was arrested when only one-half to two-thirds complete, no ethane was detected. Propylene oxidations behave similarly, with both propane and ethane being formed as products. It is clear from the results in Table 8 that the paraffin is formed in the final stages of the reaction when the supply of available oxygen has been depleted.

Table 8

OXIDATIONS OF OLEFINS AT 425° and 495°

Olefin	$\frac{[\text{oxygen}]}{[\text{olefin}]}$	extent of reaction	Temp. °C.	$\frac{100\ C_2H_6}{\text{olefin(cons)}}$	$\frac{100\ C_3H_8}{C_3H_6\text{(cons)}}$
C_2H_4	0.50	complete	425°	8	-
	0.50	2/3 complete	425	0	-
	0.50	complete	495	11	-
	0.50	2/3 complete	495	2	-
C_3H_6	0.50	complete	425	2.5	3.5
	0.50	2/3 complete	425	0	0

olefin (cons.) is the amount of olefin consumed in a run.

Hydrogen transfer to the olefin then occurs, to form an alkyl-radical. A suggested reaction is

$$C_2H_4 + HO_2 \rightleftharpoons C_2H_5 + O_2. \qquad (11)$$

When considerable oxygen is present, the equilibrium is displaced to the left, and any C_2H_5 formed will react with oxygen to reform HO_2 and ethylene. However, when the oxygen is in short supply, the alkyl radical can form an alkane by hydrogen abstraction, or, alternatively, two alkyl radicals can disproportionate to form a molecule of alkane and one of olefin.

4. COMPETITIVE ALKYLPEROXY RADICAL REACTIONS

The relative rate constants for the removal of hydrocarbon by methylperoxy, ethylperoxy, isopropylperoxy, and tert-butylperoxy radicals were calculated from

$$\frac{k_a}{k_b} = \frac{\log [R_aH]_{initial} - \log [R_aH]_{final}}{\log [R_bH]_{initial} - \log [R_bH]_{final}}$$

for eight hydrocarbon pairs. For all mixtures studied, pressure, composition, and illumination time were varied at random over as wide a range as would permit adequate consumption of reactants in a reasonable time. In no instance was k_a/k_b found to depend on the experimental conditions. An oxygen/ketone ratio of at least 3:1 was necessary to supress completely the formation of alkane and dimer corresponding to the alkyl radical formed in the ketone photolysis, and usually a much larger excess of oxygen was used.

The independence of k_a/k_b on the relative hydrocarbon concentration in the following results further justifies the use of the equation used to calculate this ratio.

A. Methane-cyclopropane Mixtures

The methane-cyclopropane system was studied at 230°

only, because at lower temperatures the consumption of hydrocarbons was too small, even with long illumination times, to permit the calculation of the rate constant ratio. The results in Table 9 show that the values of k(methane)/k(cyclopropane) are independent of the alkylperoxy radical attacking the hydrocarbon.

The absence of propylene as a reaction product indicates that under the present conditions, the isomerization of cyclopropane is negligible.

B. Cyclopropane-ethane Mixtures

The reactions of methylperoxy, ethylperoxy, isopropylperoxy, and t-butylperoxy radicals with cyclopropane-ethane mixtures at 145º and 230º have been investigated. The values of k(cyclopropane)/k(ethane) in Table 10 are independent of [cyclopropane]/[ethane] (3:1 to 1:2), [ketone]/[RH] (1.5:1 to 1:3), $[O_2]/[RH]$ (10:1 to 25:1), illumination time, and total pressure. There is a trend toward decreasing selectivity, and therefore increasing reactivity, with increasing complexity of the alkylperoxy radical, but it is doubtful whether this effect is significant.

In Figure 8, the logarithms of the rate constant ratios are plotted against the reciprocal absolute temperature. Assuming the four alkylperoxy radicals to be equivalent, the rates of consumption of cyclopropane and ethane between 145-230º are given by

$$\frac{k(\text{cyclopropane})}{k(\text{ethane})} = 0.86 \exp(-500/RT).$$

Neither ethylene nor propylene were detected among the reaction products.

C. Ethane-propane Mixtures

Ethane-propane mixtures have been reacted with methylperoxy and ethylperoxy radicals at 145º and 230º, and with

Table 9

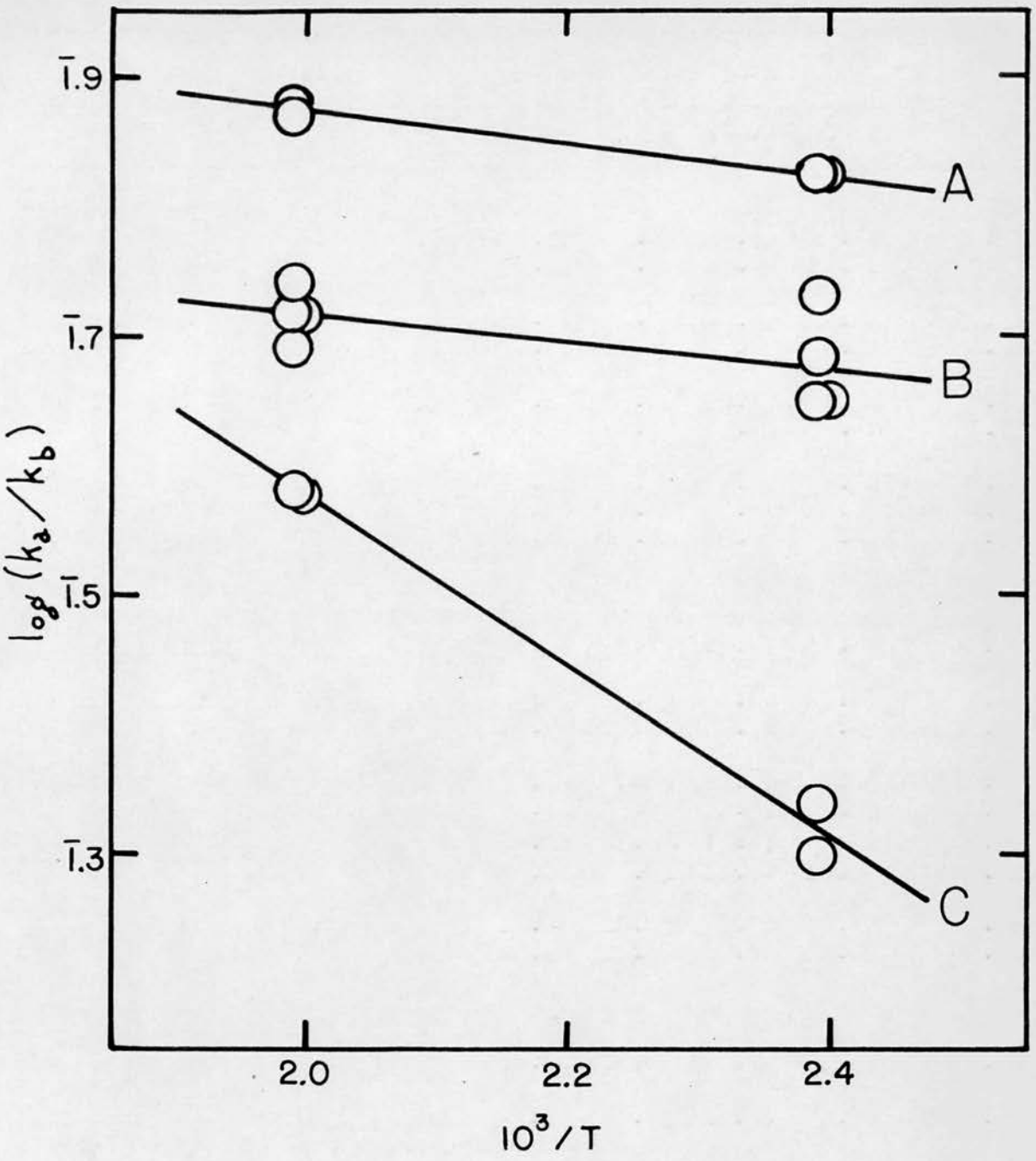
REACTIONS OF ALKYLPEROXY RADICALS WITH METHANE-CYCLOPROPANE MIXTURES AT 230°

Run N°	Exp. (min)	[Ketone] initial (mm)	$[O_2]$ initial (mm)	[Methane] initial (mm)	[Methane] final (mm)	[Cyclopropane] initial (mm)	[Cyclopropane] final (mm)	$\frac{k(\text{methane})}{k(\text{cyclopropane})}$
METHYLPEROXY								
110	105	10	350	13.23	12.86	4.07	3.48	0.17
114	180	16	415	14.30	13.81	4.40	3.55	0.15
112	375	18	270	15.67	15.22	4.83	3.60	0.10
117	150	14	360	6.44	6.32	6.06	5.09	0.12
ETHYLPEROXY								
113	180	16	215	18.51	17.77	5.69	4.18	0.13
115	230	17	430	16.90	16.20	5.20	3.68	0.12
111	270	17	300	17.88	17.40	5.52	3.92	0.08
116	180	18	415	8.96	8.68	8.44	6.23	0.11
118	200	16	350	12.88	12.10	12.12	8.52	0.17

Table 10

REACTIONS OF ALKYLPEROXY RADICALS WITH CYCLOPROPANE-ETHANE MIXTURES

Run N°	Temp. (°C)	Exp. (min)	[Ketone] initial (mm)	$[O_2]$ initial (mm)	[Cyclopropane] initial (mm)	[Cyclopropane] final (mm)	[Ethane] initial (mm)	[Ethane] final (mm)	k(cyclopropane)/k(ethane)
METHYLPEROXY									
95	145	230	23	260	6.70	6.28	13.40	11.80	0.50
92	145	340	16	160	6.97	6.12	13.93	10.41	0.45
103	145	360	13	110	9.21	8.09	3.09	2.32	0.45
100	145	445	25	315	17.07	13.85	5.73	3.48	0.42
86	230	120	8	275	5.50	4.85	11.00	8.54	0.48
88	230	120	9	240	4.30	3.64	8.60	6.02	0.47
104	230	60	16	515	15.73	13.60	5.27	4.04	0.54
108	230	120	18	190	10.18	8.30	3.41	2.19	0.47
107	230	210	18	215	16.33	12.34	5.47	3.08	0.49
ETHYLPEROXY									
97	145	345	19	340	7.93	7.32	15.87	13.55	0.48
102	145	270	27	270	14.45	12.25	4.84	3.29	0.43
101	145	360	20	435	14.08	11.56	4.72	3.05	0.45
87	230	60	8	510	6.33	5.34	12.67	9.16	0.53
89	230	60	8	205	6.03	5.18	12.07	9.03	0.52
90	230	60	4	475	5.03	4.55	10.07	8.20	0.50
91	230	60	16	405	7.80	6.27	15.60	10.18	0.51
106	230	100	17	295	16.70	12.88	5.60	3.39	0.51
105	230	115	19	445	15.20	11.30	5.10	2.95	0.53
ISOPROPYLPEROXY									
174	145	130	20	375	14.18	13.03	6.52	5.47	0.48
178	230	40	18	375	6.97	5.84	13.93	9.98	0.53
169	230	25	18	430	18.50	15.72	8.50	6.26	0.52
171	230	60	22	405	13.56	10.62	6.24	3.93	0.52
t-BUTYLPEROXY									
176	145	140	5	430	12.20	11.55	5.60	5.06	0.52
177	145	180	6	385	10.34	9.48	4.76	4.09	0.56
179	230	120	7	365	5.93	4.94	11.87	8.40	0.53
173	230	80	16	425	13.70	10.00	6.30	3.70	0.59
172	230	95	14	520	10.55	8.48	4.85	3.18	0.52



TEMPERATURE VARIATION OF RELATIVE RATE CONSTANTS FOR ALKYLPEROXY RADICAL REACTIONS

A, a = NEOPENTANE ; b = PROPANE

B, a = CYCLOPROPANE ; b = ETHANE

C, a = N-BUTANE ; b = PROPYLENE

FIGURE 8

isopropylperoxy and t-butylperoxy radicals at 230°. The values of k(ethane)/k(propane) tabulated in Table 11 are independent of [ethane]/[propane] (3:1 to 1:2), [ketone]/[RH] (1:1 to 1:3), $[O_2]$/[RH] (2:1 to 20:1), illumination time, and total pressure. There is no significant difference in the relative rates of consumption by the different alkylperoxy radicals. Within the limits of experimental accuracy, k(ethane)/k(propane) = 0.40, and is independent of temperature between 145° and 230°.

Neither ethylene nor propylene were found among the reaction products.

D. Ethane-neopentane Mixtures

The few runs carried out with the ethane-neopentane system at 230° are recorded in Table 12. The data show that k(ethane)/k(neopentane) = 0.57 at 230°, independent of whether methylperoxy or ethylperoxy radicals attack the hydrocarbon.

No olefins were present in the reaction products. The absence of isobutene implies that the pyrolysis of the neopentyl radical is negligible at 230°.

E. Neopentane-propane Mixtures

The reactions of methylperoxy and ethylperoxy radicals with neopentane-propane mixtures at 145° and 230° have been studied. The values of k(neopentane)/k(propane) in Table 13 are independent of [neopentane]/[propane] (3:1 to 1:3), [ketone]/[RH] (1:1 to 1:10), $[O_2]$/[RH] (2:1 to 20:1), illumination time, and total pressure. There is no significant difference in the relative rates of consumption of hydrocarbon by methylperoxy and ethylperoxy radicals.

The logarithms of the rate constant ratios are plotted against the reciprocal absolute temperature in Figure 8. Assuming both alkylperoxy radicals to be equivalent, the rates of consumption of neopentane and propane between 145° and 230° are given by

Table 11

REACTIONS OF ALKYLPEROXY RADICALS WITH ETHANE-PROPANE MIXTURES

Run Nº	Temp. (°C)	Exp. (min)	[Ketone] initial (mm)	[O_2] initial (mm)	[Ethane] initial (mm)	[Ethane] final (mm)	[Propane] initial (mm)	[Propane] final (mm)	k(ethane)/k(propane)
METHYLPEROXY									
65	145	175	16	450	17.72	15.10	6.18	4.07	0.38
67	145	180	15	65	11.86	10.28	4.14	2.72	0.35
69	145	240	14	100	12.90	11.02	4.50	2.83	0.34
58	145	120	17	440	7.57	6.74	15.23	11.85	0.46
60	145	180	17	140	8.37	7.42	16.83	12.10	0.37
61	145	180	12	150	7.70	6.91	15.49	11.49	0.36
63	145	210	14	260	6.70	5.62	13.50	9.21	0.46
47	230	40	15	390	16.51	14.05	5.59	3.84	0.43
49	230	50	16	80	23.60	19.35	8.00	4.94	0.41
46	230	60	19	60	26.90	22.50	9.10	5.55	0.37
48	230	125	15	355	18.60	14.00	6.30	3.12	0.41
1*	230	30	16	55	21.68	18.47	11.33	7.40	0.38
2*	230	30	10	55	13.42	11.29	7.03	4.50	0.39
3*	230	45	10	35	13.03	10.36	6.82	3.86	0.40
12*	230	30	14	40	11.42	9.76	11.46	7.46	0.37
7*	230	20	10	60	10.00	8.98	21.45	16.66	0.42
53	230	45	18	90	9.88	8.64	19.92	14.35	0.41
8*	230	55	11	55	10.28	8.46	22.05	13.71	0.41
4*	230	60	19	105	18.93	14.80	37.40	20.43	0.41
55	230	60	17	70	10.73	8.99	21.57	13.61	0.39
ETHYLPEROXY									
66	145	150	17	465	18.30	15.48	6.40	4.05	0.37
68	145	175	14	320	13.48	11.47	4.72	3.01	0.36
59	145	120	14	385	7.97	7.20	16.03	12.36	0.39
62	145	150	13	505	8.33	7.15	16.77	11.86	0.43
50	230	30	15	300	17.33	14.32	5.87	3.71	0.41
52	230	30	13	325	24.35	19.25	8.25	4.84	0.44
51	230	90	16	375	18.82	12.40	6.38	2.43	0.43
56	230	30	15	575	9.86	7.99	19.84	11.90	0.41
57	230	30	15	510	8.47	6.71	17.03	9.80	0.42
ISOPROPYLPEROXY									
181	230	50	22	285	9.14	6.45	8.96	3.93	0.42
180	230	60	19	310	15.45	11.56	15.15	7.67	0.43
t-BUTYLPEROXY									
183	230	45	5	255	8.08	6.82	7.92	5.47	0.45
182	230	75	6	280	9.04	7.21	8.86	5.33	0.44

* In these runs, samples for analysis were taken in an unpacked W trap.

Table 12

REACTIONS OF ALKYLPEROXY RADICALS WITH
ETHANE-NEOPENTANE MIXTURES AT 230°

Run N°	Exp. (min)	[Ketone] initial (mm)	$[O_2]$ initial (mm)	[Ethane] initial (mm)	[Ethane] final (mm)	[Neopentane] initial (mm)	[Neopentane] final (mm)	$\frac{k(\text{ethane})}{k(\text{neopentane})}$
METHYLPEROXY								
44	30	12	115	13.77	12.62	7.03	6.08	0.59
41	60	16	130	20.05	16.48	10.25	7.28	0.57
43	90	16	115	23.90	18.42	12.20	7.54	0.54
45	170	15	80	24.23	17.28	12.37	6.78	0.57
ETHYLPEROXY								
40	30	14	320	17.34	14.22	8.86	6.14	0.54
42	60	16	415	34.96	25.06	17.84	10.10	0.58

Table 13

REACTIONS OF ALKYLPEROXY RADICALS WITH NEOPENTANE-PROPANE MIXTURES

Run N°	Temp. (°C)	Exp. (min)	[Ketone] initial (mm)	$[O_2]$ initial (mm)	[Neopentane] initial (mm)	[Neopentane] final (mm)	[Propane] initial (mm)	[Propane] final (mm)	$\frac{k(\text{neopentane})}{k(\text{propane})}$
METHYLPEROXY									
78	145	160	14	320	3.85	2.90	11.65	7.90	0.72
75	145	260	12	160	6.08	4.94	18.32	13.57	0.69
74	145	160	14	240	11.34	9.64	3.76	2.96	0.67
70	145	165	17	70	15.47	12.86	5.13	3.81	0.63
72	145	180	15	245	10.74	8.60	3.56	2.52	0.65
23	230	30	17	65	9.28	7.76	26.70	21.05	0.76
24	230	30	15	330	9.44	7.95	27.15	21.55	0.74
27	230	30	5	70	13.27	12.30	38.13	34.08	0.68
30	230	30	20	440	29.52	24.10	9.78	7.62	0.80
31	230	30	18	75	40.57	36.40	13.43	11.50	0.72
32	230	30	19	460	28.47	22.05	9.43	6.75	0.76
35	230	30	4	205	30.20	27.45	10.00	8.77	0.73
38	230	30	16	90	16.53	13.44	5.48	4.07	0.70
ETHYLPEROXY									
76	145	180	14	180	4.04	3.14	12.16	8.36	0.67
73	145	145	15	265	11.64	10.06	3.86	3.08	0.66
71	145	180	17	365	14.34	11.23	4.76	3.32	0.67
25	230	30	19	280	10.11	7.88	29.09	20.90	0.76
26	230	30	19	95	10.16	7.71	29.24	20.15	0.75
33	230	30	18	435	32.70	23.45	10.83	7.10	0.78
34	230	30	11	70	27.35	21.90	9.04	6.86	0.78
36	230	30	8	85	27.41	22.70	9.09	7.02	0.73
37	230	30	12	155	17.05	12.59	5.65	3.80	0.76

$$\frac{k(\text{neopentane})}{k(\text{propane})} = 1.37 \exp(-600/RT).$$

No olefins were detected in the reaction products.

F. Propane-isobutane Mixtures

The experimental results for reactions of methylperoxy, ethylperoxy, isopropylperoxy, and t-butylperoxy radicals with propane-isobutane mixtures at 145° and 230° are presented in Table 14. The values of k(propane)/k(isobutane) are independent of [propane]/[isobutane] (3:1 to 1:3), [ketone]/[RH] (1:1 to 1:4), $[O_2]$/[RH] (10:1 to 25:1), illumination time and total pressure. There is no significant difference in the relative rates of consumption of hydrocarbons by the different alkylperoxy radicals. Within the limits of experimental error, k(propane)/k(isobutane) = 0.70, and is independent of temperatures between 145° and 230°.

Neither propylene nor isobutene were detected among the reaction products.

G. Propane-n-butane Mixtures

The experimental results for reactions of methylperoxy and ethylperoxy radicals with mixtures of propane and n-butane at 145° and 230° are presented in Table 15. Within the limits of experimental error, k(propane)/k(n-butane) = 0.60 for hydrocarbon attack by both methylperoxy and ethylperoxy radicals, and is independent of the ratio of propane to n-butane between 3:1 and 1:2 and of the temperature between 145° and 230°.

No olefins were detected in the reaction products.

H. n-Butane-propylene Mixtures

The reactions of methylperoxy and ethylperoxy radicals with n-butane-propylene mixtures at 145° and 230° have been studied. The values of k(n-butane)/k(propylene) presented in Table 16 are independent of changes in the ratio of n-butane

Table 14

REACTIONS OF ALKYLPEROXY RADICALS WITH PROPANE-ISOBUTANE MIXTURES

Run N°	Temp. (°C)	Exp. (min)	[Ketone] initial (mm)	[O_2] initial (mm)	[Propane] initial (mm)	[Propane] final (mm)	[Isobutane] initial (mm)	[Isobutane] final (mm)	$\frac{k(propane)}{k(isobutane)}$
METHYLPEROXY									
128	145	120	12	320	12.13	9.34	3.87	2.74	0.73
126	145	180	17	305	19.56	14.38	6.24	4.00	0.69
134	145	225	16	230	6.07	4.47	18.83	11.81	0.67
123	230	30	14	425	13.95	11.49	4.45	3.42	0.73
121	230	60	16	230	16.91	11.65	5.39	3.02	0.65
130	230	30	14	345	4.14	3.33	12.86	9.38	0.69
132	230	45	21	400	4.71	3.39	14.59	9.00	0.69
ETHYLPEROXY									
127	145	120	18	370	16.22	12.33	5.18	3.52	0.71
125	145	170	17	320	15.47	10.71	4.93	2.91	0.70
133	145	130	16	365	4.54	3.46	14.06	9.45	0.69
124	230	25	17	355	12.74	8.36	4.06	2.23	0.70
122	230	45	17	420	17.73	9.47	5.67	2.32	0.70
131	230	20	18	325	6.14	4.66	19.06	12.92	0.71
129	230	30	16	315	4.20	2.69	13.00	6.85	0.70
ISOPROPYLPEROXY									
193	145	60	20	400	9.56	8.96	10.44	9.35	0.67
184	230	30	19	400	11.10	7.14	11.00	5.96	0.72
187	230	30	15	415	10.83	4.97	10.77	3.96	0.77
190	230	30	15	300	9.32	5.80	10.18	5.23	0.71
t-BUTYLPEROXY									
194	145	100	6	355	10.12	9.27	11.08	9.75	0.68
191	230	45	5	415	9.08	7.60	9.92	7.65	0.69
192	230	50	6	375	6.16	4.66	6.74	4.49	0.69
185	230	60	5	395	12.12	7.77	12.08	6.48	0.72

Table 15

REACTIONS OF ALKYLPEROXY RADICALS WITH PROPANE-n-BUTANE MIXTURES

Run N°	Temp. (°C)	Exp. (min)	[Ketone] initial (mm)	$[O_2]$ initial (mm)	[Propane] initial (mm)	[Propane] final (mm)	[n-Butane] initial (mm)	[n-Butane] final (mm)	$\frac{k(\text{propane})}{k(\text{n-butane})}$
METHYLPEROXY									
146	145	145	23	260	6.49	4.90	13.11	8.12	0.59
153	230	30	11	355	14.71	12.22	4.89	3.68	0.64
151	230	30	20	395	20.50	16.36	6.80	4.67	0.60
144	230	30	19	265	7.19	5.53	14.51	9.42	0.60
142	230	35	22	345	6.78	4.66	13.72	7.57	0.63
149	230	50	14	200	7.29	4.87	14.71	7.45	0.59
ETHYLPEROXY									
147	145	90	17	260	6.03	5.01	12.17	9.21	0.65
145	145	130	16	325	5.87	4.60	11.83	7.70	0.57
152	230	30	18	390	20.20	13.38	6.70	3.38	0.61
150	230	40	17	395	15.77	9.05	5.23	2.05	0.59
148	230	35	21	235	7.68	4.28	15.51	5.74	0.59
143	230	25	19	385	6.03	3.85	12.17	5.72	0.60

Table 16

REACTIONS OF ALKYLPEROXY RADICALS WITH n-BUTANE-PROPYLENE MIXTURES

Run N°	Temp. (°C)	Exp. (min)	[Ketone] initial (mm)	$[O_2]$ initial (mm)	[n-Butane] initial (mm)	[n-Butane] final (mm)	[Propylene] initial (mm)	[Propylene] final (mm)	$\frac{k(n\text{-butane})}{k(propylene)}$
METHYLPEROXY									
164	145	85	18	335	13.12	12.18	6.28	3.92	0.16
161	145	245	19	195	15.68	9.85	7.52	1.04	0.23
168	145	115	22	240	6.66	5.67	13.84	6.16	0.20
157	230	25	22	230	14.06	9.10	6.74	2.19	0.39
159	230	35	17	280	20.35	14.30	9.75	3.61	0.36
166	230	30	20	220	8.09	6.30	16.81	8.76	0.38
ETHYLPEROXY									
160	145	60	18	360	14.06	12.78	6.74	3.98	0.18
163	145	95	17	330	12.37	10.67	5.93	3.13	0.23
162	145	190	16	355	13.11	8.34	6.29	0.89	0.23
167	145	115	20	500	8.71	7.15	18.09	7.75	0.23
156	230	30	19	415	13.52	5.30	6.48	0.63	0.40
158	230	30	18	450	11.83	6.55	5.67	1.18	0.38
165	230	30	18	295	10.55	7.85	21.95	9.72	0.37

to propylene between 2:1 and 1:2. There is no significant difference in the relative rates of consumption of hydrocarbon by methylperoxy and ethylperoxy radicals.

The logarithms of the rate constant ratios are plotted against reciprocal absolute temperature in Figure 8. Assuming both alkylperoxy radicals to be equivalent, the rates of consumption of n-butane and propylene between 145º and 230º are given by

$$\frac{k(\text{n-butane})}{k(\text{propylene})} = 7.8 \exp(-3000/RT).$$

I. Hydrogen-methane Mixtures

Attempts to react methylperoxy radicals with hydrogen-methane mixtures at 230º were unsuccessful. Consumption of methane was very small and that of hydrogen was negligible. The failure of hydrogen to be consumed is probably due in part to its low reactivity, and in part to the reformation of the hydrogen molecule by abstraction by the hydrogen atom when formed. The oxidation of a hydrogen atom

$$H\cdot + O_2 + M \longrightarrow HO_2 + M \qquad (12)$$

is highly exothermic, and requires a third body to absorb the excess energy. It is likely that abstraction will occur before the hydrogen atom is thus removed.

5. PHOTOLYSIS OF ISOBUTANE-ACETONE-OXYGEN MIXTURES

Two mixtures of isobutane-acetone-oxygen were photolysed at 230º. The quantity of isobutane consumed and of CO produced were determined, the later value being taken as measure of the amount of ketone decomposed by photolysis,

$$(CH_3)_2CO + h\nu \longrightarrow CH_3\cdot + CH_3CO\cdot \qquad (5a)$$

$$CH_3CO\cdot \longrightarrow CH_3\cdot + CO \qquad (6a)$$

and hence the maximum number of methylperoxy radicals generated,

$$CH_3\cdot + O_2 \longrightarrow CH_3OO\cdot \quad . \qquad (7a)$$

For comparison, and to show that CO was not produced by the oxidative degradation of isobutane or alkyl radicals, photolyses of acetone were performed under identical conditions, but with no oxygen or isobutane in the reaction mixture. The results presented in Table 17 show that at 230°

$$\frac{\text{isobutane consumed}}{\text{alkyl radicals from ketone}(=2CO)} \simeq 0.6 \quad .$$

At 145°, the rate of hydrocarbon consumption in the competitive reactions is approximately one-fifth that at 230°, conditions other than temperature being similar. Therefore at 145°,

$$\frac{\text{isobutane consumed}}{\text{alkyl radicals from ketone}(=2CO)} \simeq 0.1 \quad .$$

Since isobutane is the most reactive of the hydrocarbons used, the ratio of hydrocarbon consumed to alkyl radicals produced is always less than this value.

Table 17

PHOTOLYSES OF ISOBUTANE-ACETONE-OXYGEN MIXTURES AT 230°

Run N°	Exp. (min)	[Acetone] initial (mm)	$[O_2]$ initial (mm)	[Isobutane] initial (mm)	[Isobutane] final (mm)	[Isobutane] consumed (mm)	[CO] produced (mm)
199	32	19.0	107	22.9	15.2	7.7	6.1
202	32	20.1	98	20.6	14.5	6.1	5.7
200	32	19.0	-	-	-	-	5.7
201	32	19.4	-	-	-	-	5.4

6. PRODUCTION OF PERHYDROXY RADICALS

Attempts were made to produce perhydroxy radicals (HO_2) by the photolysis of formaldehyde in the presence of excess oxygen :

$$H_2CO + h\nu \longrightarrow H + HCO \qquad (5b)$$

$$HCO \longrightarrow H + CO \qquad (6b)$$

$$H\cdot + O_2 \longrightarrow HO_2\cdot \qquad (7b)$$

Reaction (7b) is highly exothermic[43], $\Delta H \geq 46$ kcal mole^{-1} and in the absence of an effective third body (reaction (12)) HO_2 will not form. When hydrocarbon was added to the reaction system, the rate of consumption was small, and extremely unreproducible results were obtained. Similar hydrocarbon consumptions were obtained in the absence of oxygen. All attack appears to be by hydrogen atoms or formyl radicals, rather than by HO_2, and these experiments had to be abandoned.

DISCUSSION

1. THE OXIDATION OF SATURATED HYDROCARBONS

The developement of an unequivocal theory of hydrocarbon oxidation has been hindered by the complexity of the overall reaction. It is accepted today that hydrocarbon oxidations follow the pattern of a degenerately branching free-radical chain mechanism[5], which accounts for the characteristic induction period followed by an exponential increase in reaction rate leading either to ignition, or to a fall off in rate to zero. The identification of the elementary reactions in such a mechanism is extremely difficult, because methods must be found to isolate the various factors, such as chain initiation, branching, propagation, and termination, which contribute to the overall reaction.

The results of Knox, Smith, and Trotman-Dickenson[13] and of the present work[a] of the measurement of rates of disappearance of two hydrocarbons, R_aH and R_bH, in a mixed oxidation pertain only to the chain-propagating reactions,

$$X_1 + R_aH \xrightarrow{k_{a1}} X_1H + R_a \qquad (1)$$

$$X_2 + R_bH \xrightarrow{k_{b2}} X_2H + R_b \qquad (2)$$

$$X_2 + R_aH \xrightarrow{k_{a2}} X_2H + R_a \qquad (3)$$

$$X_1 + R_bH \xrightarrow{k_{b1}} X_1H + R_b \qquad (4)$$

where $R_a \longrightarrow X_1$ and $R_b \longrightarrow X_2$

as these are the reactions principally responsible for the consumption of hydrocarbons.

The invariance of the rate constant ratios, k_a/k_b, with the relative concentration of the two hydrocarbons in the mixture indicates that the reactivities of the chain-propagating radicals derived from different hydrocarbons are identical. In terms of the above mechanism, $k_{a1} = k_{a2}$ and $k_{b1} = k_{b2}$ between 328º and 495º, and at all ratios of oxygen to hydrocarbon, even when the value of k_a/k_b depends upon $[O_2]/[RH]$.

The effect of increasing the oxygen concentration in a mixture undergoing oxidation is basically to increase the extent of reaction, and thereby to alter the nature of the end products. The variation of the oxygen concentration in the oxidation of propane between 320º and 480º has been shown to have little effect on the yields of major products formed in the initial stages of the reaction[9,44]. Therefore the effect of increasing $[O_2]/[RH]$ on k_a/k_b at the higher temperatures does not necessarily reflect a change in the initial rates of removal of the two hydrocarbons. It is more likely that the rates of removal in the later stages of the reaction differ. This implies that the nature of the radical, or radical mixture, which attacks the hydrocarbons, changes as the reaction proceeds at these temperatures.

Falconer and Knox[9] found that at least two mechanisms operate in the high temperature oxidation of propane, the mechanism depending upon the temperature and the degree of advancement of the reaction. Szabo and Gál[45] have also found two types of reaction in the high temperature oxidation of ethane, one at oxygen concentrations below 30 per cent, and the other at higher oxygen concentrations. They conclude that the differences in the two mechanisms are either in the chain-initiating or the chain-propagating reactions. The present results indicate that a change in the mechanism of the chain-propagating reaction with oxygen concentration occurs at temperatures above about 350º, caused by a change in the nature of the chain-carrying radical with oxygen concentration, i.e. with the extent of reaction.

The relative rate constants for the radical operative during the initial stages of hydrocarbon oxidations have been determined by extrapolating the values of k_a/k_b obtained experimentally to zero oxygen concentration. The relative reactivities thus obtained have been extrapolated to 230º and are compared in Table 18 with the relative reactivities of other radicals which have been studied in competitive systems[31,34-36,46-48,b].

Although the identity of the radical responsible for hydrocarbon consumption in the initial stages of oxidations is uncertain, there is little doubt that it is an oxygenated radical such as OH, HO_2, RO, or RO_2. From Table 18 it can be seen that it is a reactive radical, comparable in reactivity with small oxygenated radicals. Its reactivity with saturated hydrocarbons closely resembles the reactivities of the four alkylperoxy radicals.

There is considerable independent evidence that HO_2 plays an important role in the oxidation of hydrocarbons at higher temperatures. It is difficult to explain the formation of propylene without hydrogen as the major initial product in the oxidation of propane above 400º, as found by Falconer and Knox[9], and Satterfield and Wilson[10], without accepting the following reactions :

$$C_3H_7 + O_2 \longrightarrow C_3H_6 + HO_2 \qquad (10a)$$

$$HO_2 + C_3H_8 \longrightarrow C_3H_7 + H_2O_2 \,. \qquad (13)$$

The high conversion of ethane to ethylene in oxygen weak ethane oxidations found here at 495º, and the high conversion to ethylene found by Knox and Wells[42] in the oxidation of ethane at 360º point to the following chain :

$$C_2H_5 + O_2 \longrightarrow C_2H_4 + HO_2 \qquad (10b)$$

$$C_2H_6 + HO_2 \longrightarrow C_2H_5 + H_2O_2 \,. \qquad (13a)$$

Table 18

RELATIVE REACTIVITIES OF SATURATED HYDROCARBONS

Radical	Temp. (°C)	Relative Reactivity							Refs.
		Methane	Ethane	Propane	Cyclo-propane	n-Butane	Iso-butane	Neo-pentane	
F	25	0.6	1	1.4	0.9	1.6	1.7	1.8	46
Cl	250	0.02	1	2.0	0.03	3.0	2.2	2.1	36
OH	18	-	1	2.8	0.18	3.7	3.1	-	35
Oxid* ..	230	0.05	1	2.2	0.50	-	3.2	1.5	a
MeOO ..	230	0.06	1	2.5	0.49	4.1	3.6	1.8	b
EtOO ..	230	0.06	1	2.4	0.52	4.1	3.5	1.8	b
i-PrOO.	230	-	1	2.3	0.52	-	3.2	-	b
t-BuOO.	230	-	1	2.2	0.54	-	3.2	-	b
CF_3 ...	182	0.05	1	3.0	-	5	7.5	1.5	47
MeO ...	230	-	1	3.6	0.35	6.4	5.9	1.9	34
Me	182	0.03	1	3.3	0.55	5.7	10	1.7	31
Br	98	0.002	1	43	-	200	1050	0.75	48

* "Oxid" refers to the chain-carrying radical in oxidation when $[O_2]/[RH] = 0$.

The formation of olefins corresponding to the original hydrocarbons as the major initial products in the competitive oxidations is explained by reactions analagous to (10) and (13). An HO_2 chain has been proposed at temperatures as low as 270° to explain the formation of acetaldehyde and hydrogen peroxide in equal amounts as the only products in the early stages of the oxidation of ethyl alcohol[49],

$$C_2H_5O + O_2 \longrightarrow CH_3CHO + HO_2$$

$$HO_2 + C_2H_5OH \longrightarrow C_2H_5O + H_2O_2 .$$

The formation of the corresponding alkane in the final stages of the oxidation of ethylene and propylene above 425° is further evidence that HO_2 radicals are important as chain-propagators ;

$$C_2H_4 + HO_2 \longrightarrow C_2H_5 + O_2 \qquad (11)$$

$$C_2H_5 + (RH, \text{ etc.}) \longrightarrow C_2H_6 + (R^{\cdot}, \text{ etc.})$$

The differences in reactivity of the four alkylperoxy radicals that have been investigated are small (see Table 18), and probably fall within the experimental error. Since the reactivity of ROO is unaffected by a change of R when R is an alkyl radical, it is unlikely that if R were a hydrogen atom the reactivity would change greatly. This equivalence would be expected on general grounds, as the position where the radical is changed is relatively far from the active center of the radical, and hence the ROO-H bond strength should not depend greatly on the nature of R. Although the relative reactivities of hydrocarbons with HO_2 have not been measured directly, as a good approximation they may be considered to be the same as those with alkylperoxy radicals, and therefore to resemble closely the relative reactivities with the radical responsible for chain-propagation in the initial stages of hydrocarbon oxidation.

The identification of the oxidation radical as HO_2 suffers from the difficulty that the currently accepted value for the strength of the first O-H bond in hydrogen peroxide is that of Foner and Hudson[50], D(HOO-H) = 89.5 ± 3 kcal mole^{-1}, Accepting this value, the reactions of HO_2 with saturated hydrocarbons would be considerably endothermic, and as a consequence, activation energy differences of several kilocalories would be expected between the various hydrocarbons. The small activation energy differences observed indicate a radical that forms a bond of about 100 kcal mole^{-1} with a hydrogen atom. Furthermore, the reactivities of the alkylperoxy radicals also indicate that D(ROO-H) should be about 100 kcal mole^{-1}, and it is unlikely that D(ROO-H) is 10 kcal mole^{-1} greater than D(HOO-H). The earlier value of D(HOO-H) = 102 kcal mole^{-1}, given by Evans, Hush, and Uri[51], would make the reactions of HO_2 (and also RO_2) with hydrocarbons slightly exothermic, and would thus be in better agreement with the small activation energy differences found for the chain-propagating reactions.

Although the reactivities of alkylperoxy radicals parallel those found for the initial chain-propagating radical in oxidations, alkylperoxy radicals are unlikely to carry the chains in the temperature range of thermal oxidations. The initial products formed by an alkylperoxy chain would be hydroperoxides. Kirk and Knox[52] have shown that hydroperoxides cannot be important as branching intermediates in oxidations because of their short lifetimes. If formed in quantity, they would cause a rapid acceleration through their chain branching homogeneous decomposition

$$ROOH \longrightarrow RO + OH \cdot$$

Hydroperoxides are not found as initial products of thermal oxidations, and neither their homogeneous nor heterogeneous decompositions[12] produce quantities of olefin comparable to those produced in the early stages of oxidation[9,10,42,a] at temperatures above 320°. The reactions of alkylperoxy radicals at lower temperatures have been found to yield no olefin products.

In the initial stages of photochemically initiated oxidations of simple hydrocarbons at low temperatures, Nalbandyan and Fok[53] have found peroxides to be the sole primary products. But as the temperature is raised, aldehydes are produced as primary products at the expense of peroxides, and at about 300° the formation of peroxides ceases. Semenov[54] proposes that at low enough temperatures an alkylperoxy chain predominates

$$R + O_2 \longrightarrow ROO \qquad (7)$$

$$ROO + RH \longrightarrow ROOH + R \qquad (8,9)$$

but as the temperature is increased, isomerization reactions of the peroxy radical, having greater activation energies, increase in importance. Except for methane, these isomerizations, which are immediately followed by decomposition, can occur either by C-H bond rupture, or C-C bond rupture, and thus lead to the formation of a large number of products and radicals, e.g., for propane :

$$CH_3\text{-}\underset{\underset{O\text{-}O}{|}}{CH}\text{-}CH_3 \longrightarrow CH_3\text{-}\underset{\underset{O\text{-}O}{|}}{CH}\ CH_3 \longrightarrow CH_3CHO + CH_3O \qquad (14)$$

$$CH_3\text{-}\underset{\underset{O\text{-}O}{|}}{CH}\text{-}\underset{H}{CH_2} \longrightarrow CH_3\text{-}\underset{\underset{O\text{-}O}{|}}{CH}\text{-}CH_2 \longrightarrow CH_3CH{=}CH_2 + HO_2 \qquad (15)$$

$$CH_3\text{-}\underset{\underset{O\text{-}O}{|}}{CH}\text{-}CH_3 \longrightarrow CH_3\text{-}\underset{\underset{O\text{-}O}{|}}{C}\text{-}CH_3 \longrightarrow CH_3COCH_3 + OH \qquad (16)$$

$$CH_3\text{-}\underset{\underset{O\text{-}O}{|}}{CH}\text{-}\underset{H}{CH_2} \longrightarrow CH_3\text{-}CH\text{-}CH_2 \longrightarrow CH_3CH{=}CH_2 + HO_2 \qquad (17)$$

$$\underset{H}{CH_2}\text{-}CH_2\text{-}\underset{\underset{O\text{-}O}{|}}{CH_2} \longrightarrow CH_2\text{-}CH_2\text{-}\underset{\underset{H\text{-}O\text{-}O}{|}}{CH_2} \longrightarrow CH_2{=}CH_2 + CH_2O + OH \qquad (18)$$

$$CH_3\text{-}CH_2\text{-}\underset{\underset{O\text{-}O}{|}}{CH_2} \longrightarrow CH_3\underset{\underset{O\text{-}O\text{-}H}{|}}{CH_2}CH \longrightarrow CH_3CH_2CHO + OH \qquad (19)$$

Large quantities of propionaldehyde are not reported as initial products in propane oxidations[9,55], but acetaldehyde, formaldehyde, and olefins are all found. On this basis, reaction (19) appears less important than the others.

Knox and Wells[42] have recently found that in the oxidation of ethane the conversion to ethylene falls to 50 per cent at 320° from 80 per cent at 360° and above. The ethylene is replaced as a product not by an increase in acetaldehyde, but by an increase in formaldehyde. The increase in formaldehyde is less at low oxygen concentrations. Considering reactions analagous to (14) to (19),

$$CH_3\underset{\underset{O\text{-}O}{|}}{CH_2} \longrightarrow CH_3\,\underset{O\text{-}O}{\diagdown\!\diagup}\,CH_2 \longrightarrow CH_2O + CH_3O \qquad (20)$$

$$\underset{H}{\diagup}CH_2\underset{\underset{O\text{-}O}{|}}{CH_2} \longrightarrow CH_2\text{-}\underset{\underset{H\text{-}O\text{-}O}{|}}{CH_2} \longrightarrow CH_2{=}CH_2 + HO_2 \qquad (21)$$

$$CH_3\text{-}\underset{\underset{O\text{-}O}{|}}{CH_2} \longrightarrow CH_3\text{-}\underset{\underset{O\text{-}O}{|}}{CH}\,H \longrightarrow CH_3CHO + OH \qquad (22)$$

it appears that with lowering the temperature, reaction (21) becomes less important, and is replaced not by (22) which gives acetaldehyde as product, but by (20) producing formaldehyde.

In the presence of sufficient oxygen, the methoxyl radicals formed via reaction (20) (or with propane, reaction (14)) are oxidized to more formaldehyde.

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \qquad (23)$$

Methoxyl radicals formed in these reactions, and OH radicals, formed in reactions (18), (19), and (22) cannot be important chain-carriers in the early stages of hydrocarbon oxidation as their reactivities[34,35] are not the same as those of the chain-propagating radicals in oxygen weak mixtures.

The isomerization reactions (15), (17), and (21) are individual cases of the olefin forming reaction (10)

$$R + O_2 \longrightarrow \text{olefin} + HO_2 \qquad (10)$$

which appears to have a lower temperature limit about the bottom of the thermal oxidation range.

Accepting a higher activation energy for the isomerization-decomposition reactions of ROO than for the abstraction reaction, this activation energy is likely to be higher for those reactions producing olefin and HO_2 than for those having an aldehyde and a methoxyl radical as product, because the former are about 50 kcal $mole^{-1}$ less exothermic.

Alkylperoxy radicals, then, because of their isomerization, and because an alkylperoxy chain does not produce large amounts of olefin, appear to be improbable chain-carriers in the thermal oxidation range, but the experimental evidence indicates that at lower temperatures (below about 250º) alkylperoxy abstractions are important, giving large initial yields of hydroperoxide. As the temperature increases toward the thermal range, isomerization, followed by decomposition, of the alkylperoxy radical appears to occur, producing an inferior aldehyde and a methoxy radical, which, in the presence of sufficient oxygen, is in turn oxidized to formaldehyde and HO_2. At normal oxidation temperatures, there is abundent evidence that the olefin forming HO_2 chain predominates, say from 300º to 500º, either with or without the formation of an alkylperoxy radical as an intermediate step.

The properties of the radical or radicals responsible for the removal of hydrocarbon in the later stages of oxidation

at higher temperatures (above 350°) are not well defined. Its relative reactivity could not be determined in the competitive oxidations because at accessible oxygen concentrations, the ratio k_a/k_b had not attained a steady value which would have been characteristic of this radical. The later stage radical appears, however, to be somewhat more reactive than that which consumes hydrocarbon in the initial stages of an oxidation. It is probably formed from the secondary oxidation of a product of the initial reaction.

Studies of ethane[42] and propane[9,44] oxidations show that a major feature of the oxidation in the later stages is the removal of olefin. Olefins react much faster than paraffins of the same carbon number. It was therefore possible that the addition of olefin to the reaction mixture could induce behaviour characteristic of a mature reaction in the initial stages of an oxidation. Experiments in which ethylene and propylene were added to ethane-propane mixtures showed that this was not the case. Even the addition of acetaldehyde had no effect on the relative rate constants, except when added in very large quantity. The identity of the product from which the later stage radicals are formed is still unknown.

Because there is no dependence of the relative rates of hydrocarbon consumption upon the relative concentrations of the two hydrocarbons, even when the oxygen to hydrocarbon ratio is large, the important radicals at this stage are not characteristic of the hydrocarbons from which they are formed. Since this applies even in methane-ethane mixtures, it is unlikely that the radical contains more than one carbon atom. The possibilities are therefore limited to OH, CHO, CH_3, CH_3O, and CH_3OO radicals, if HO_2 is to be accepted as the radical operative in the initial stages of the oxidation. The absence of methane as a product, except at the very end of the reactions, indicates that methyl radicals are oxidized before they have time to abstract. The formation of methanol[56-57] suggests that methoxyl radicals are present, but the relative reactivities of hydrocarbons with

them[34], as with methyl radicals[31], do not correspond to those observed. The low strength of the H-CHO bond eliminates formyl radicals. Alkylperoxy radicals have reactivities corresponding to the radical of the initial stages, and so methylperoxy cannot be responsible for the change in rates of consumption in the later stages of high temperature oxidations. Therefore, hydroxyl radicals appear to be the most probable chain carriers in this region. Bercés and Trotman-Dickenson[35] have found the relative reactivities of hydrocarbons with OH at 18º to be very similar to those with chlorine atoms at the same temperature. The OH radicals is small, and its reactions with hydrocarbons are considerably exothermic. Therefore its properties fit the requirements for the chain propagating radicals in the later stages of high temperature hydrocarbon oxidation.

If the decomposition of hydroperoxide cannot be an important source of OH, two further sources may be considered which could produce this radical in the later stages of reaction at higher temperatures. Hydrogen peroxide, a product of the HO_2 chain in the initial stages, decomposes homogeneously into two hydroxyl radicals,

$$HOOH \longrightarrow 2OH \qquad (24)$$

This reaction, which is about 50 kcal $mole^{-1}$ endothermic, would be in competion with the wall destruction of the hydrogen peroxide. The average lifetime of a hydrogen peroxide molecule undergoing homogeneous decomposition at 435º is about 90 seconds[58], whereas at 475º this value reduces to about 10 seconds. Diffusion to the wall of the reaction vessel under average conditions will take 2-3 seconds. Thus reaction (24) is unlikely to compete effectively with wall destruction much below 475º, but above this temperature, it should become an important branching reaction.

Hydroxyl radicals could also arise by the isomerization-decomposition reactions of alkylperoxy radicals, (e.g., reactions (16), (18), (19), and (22)), or equally by the analagous reactions

of alkyl radicals with oxygen, without the alkylperoxy intermediate. Although these reactions are about 50 kcal mole^{-1} more exothermic than the corresponding reactions yielding HO_2 and olefin, eg. for ethane

$$C_2H_5 + O_2 \longrightarrow CH_3CHO + OH \qquad (\Delta H = -56) \qquad (25)$$

$$C_2H_5 + O_2 \longrightarrow C_2H_4 + HO_2 \qquad (\Delta H = -6) \qquad (26)$$

they do not appear to be important in the initial stages or at lower temperatures (below 350º) for reasons already cited. However, with methyl radical oxidations, reaction (27) is about 90 kcal mole^{-1} more exothermic than reaction (28),

$$CH_3 + O_2 \longrightarrow CH_2O + OH \qquad (\Delta H = -50) \qquad (27)$$

$$CH_3 + O_2 \longrightarrow CH_2 + HO_2 \qquad (\Delta H = 43) \qquad (28)$$

Methyl radicals, when formed, are oxidized, as is shown by the lack of formation of methane by abstraction reactions, except at the very end of an oxidation. The absence of methyl hydroperoxide as a product indicates that methylperoxy radicals do not abstract at these temperatures. Therefore reaction (27), which is a non-branching reaction, could become important at temperatures high enough to supply the energy required for activation. It would not be expected to be important in the initial stages of the reaction, as it should roughly parallel the rate of formation of methyl radicals by hydrocarbon degradation.

2. TRANSFER REACTIONS OF ALKYLPEROXY RADICALS AND OF THE OXIDATION CHAIN RADICAL

Despite the considerable attention that radical transfer reactions

$$A + BC \longrightarrow AC + B$$

have received, full investigationsof only a relatively few atoms and radicals have been made. Most of these investigations have consisted of a study of the abstraction of hydrogen atoms from a series of substrates HB, HB' , HB'' etc. by the radical A. The abstraction of hydrogen from a saturated hydrocarbon by an alkylperoxy radical

$$ROO + RH \longrightarrow ROOH + R \qquad (8,9)$$

falls into this class of reactions, as does the chain-propagating radical in the oxidation of saturated hydrocarbons,

$$X + RH \longrightarrow XH + R \qquad (1\text{-}4)$$

where a hydrogen atom is transfered from the substrate molecule RH to an oxygenated radical X.

The obstacles to the determination of radical concentrations have led many workers to adopt competitive methods to determine the relative rate constants for two hydrocarbons reacting with a single radical in the same reaction system. As the radical concentration [A] will be the same for both reactions,

$$A + BH \longrightarrow AH + B$$

$$Rate_{BH} = k_{BH}[A]\ [BH]$$

$$A + B'H \longrightarrow AH + B'$$

$$Rate_{B'H} = k_{B'H}[A]\ [B'H]$$

the relative rate constants can be found by division

$$\frac{k_{BH}}{k_{B'H}} = \frac{Rate_{BH}}{Rate_{B'H}} \cdot \frac{[B'H]}{[BH]}$$

if the progress of the reaction can be followed suitably. Two methods have been used ; either the amounts of each hydrocarbon

consumed, or the amounts of characteristic products formed from each can be measured. If products are measured, then the extent of reaction is measured directly, and the products may be characteristic of radical attack at various points on the substrate molecule. Despite these two advantages, the difficulty of isolating products truly characteristic of each hydrocarbon to provide an accurate measure of their disappearance has necessitated the following of the reactions by measurements of hydrocarbon consumption in the present experiments.

The relative rate constants may be plotted on the usual Arrhenius plot of $\ln(k_{BH}/k_{B'H})$ against the reciprocal absolute temperature, whence the slope of the line will equal $-(E_{BH}-E_{B'H})/RT$, and the intercept will be $\ln(A_{BH}/A_{B'H})$. If many hydrocarbons, BH, B'H, B''H, etc. are taken stepwise in pairs, then the Arrhenius parameters of the whole series of reactions can be calculated if those for any one reaction can be determined independently.

Unfortunately, the rate constants for hydrogen abstractions by most radicals and atoms have been determined for attack on the hydrocarbon molecule as a whole. This gives only an average value for the rates of attack on all the C-H bonds in the molecule, which limits the usefullness of the measurements, as there is no doubt that different C-H bonds, primary, secondary, tertiary, etc. react at different rates[59].

With chlorine[36] and bromine[46] atoms, and with methyl radicals[31], it has been found that the reactivity does not vary greatly from one hydrocarbon to another for bonds of a given order. It is therefore reasonable to assume that for other radicals the reactivity of C-H bonds of a given order are identical for all hydrocarbons, and hence to calculate the relative rate constants per hydrogen atom from the data in Table 18. An example, using the data for methylperoxy radicals at 230° will illustrate these calculations.

Rate of attack on primary H atoms :

$$\text{For ethane} = \frac{\text{relative rate constant}}{\text{no. of H atoms}}$$

$$= \frac{1.00}{6}$$

$$= 0.167$$

$$\text{For neopentane} = \frac{\text{relative rate constant}}{\text{no. of H atoms}}$$

$$= \frac{1.80}{12}$$

$$= 0.150$$

Mean = 0.159

Rate of attack on secondary H atoms

$$\text{For propane} = \frac{\text{rel. rate constant} - 6 \times \text{primary H atom}}{\text{no. of secondary H atoms}}$$

$$= \frac{2.5 - (6 \times 0.16)}{2}$$

$$= 0.77$$

$$\text{For n-butane} = \frac{\text{rel. rate constant} - 6 \times \text{primary H atom}}{\text{no. of secondary H atoms}}$$

$$= \frac{4.1 - (6 \times 0.16)}{4}$$

$$= 0.76$$

Mean = 0.765

Rate of attack on tertiary H atoms :

For isobutane = rel. rate constant - 9 x primary H atom

$= 3.6 - (9 \times 0.16)$

$= 2.16$

Rate of attack on cyclopropyl H atoms :

$$\text{For cyclopropane} = \frac{\text{relative rate constant}}{\text{no. of H atoms}}$$

$$= \frac{0.49}{6}$$

$$= 0.082$$

Rate of attack on methyl H atoms :

$$\text{For methane} = \frac{\text{relative rate constant}}{\text{no. of H atoms}}$$

$$= \frac{0.06}{4}$$

$$= 0.015$$

Therefore :

Type of H atom	Methyl	Cyclo-propyl	Primary	Secondary	Tertiary
Rel. rate constant per H atom at 230°	0.015	0.082	0.159	0.77	2.16
Relative to primary ...	0.10	0.52	1.00	4.8	13.4

The reactivities per hydrogen atom calculated in this way for the chain-propagating radical in the early stages of oxidation and for the four alkylperoxy radicals that have been studied, are compared in Table 19 with those found for other radicals[31,34-36,46-48]. The expected trend in the direction of

Table 19

RELATIVE REACTIVITIES OF HYDROGEN ATOMS

Radical	Temp. (°C)	Type of H atom					E(ethane)**	Refs.
		Methyl	Cyclo-propyl	Primary	Secondary	Tertiary		
F	25	0.8	0.9	1	1.2	1.4	0.3	46
Cl	250	0.03	0.03	1	3	3	1.0	36
OH	18	-	0.18	1	4.7	9.8	-	35
Oxid* .	230	0.09	0.52	1	4.5	13.2	-	a
MeOO ..	230	0.10	0.52	1	4.8	13.4	-	b
EtOO ..	230	0.10	0.55	1	4.6	12.4	-	b
i-PrOO.	230	-	0.52	1	4.0	13.2	-	b
t-BuOO.	230	-	0.54	1	3.7	13.1	-	b
CF_3 ...	182	0.08	-	1	6	36	7.5	47
MeO ...	230	-	0.35	1	8	27	7.1	34
Me	182	0.04	0.55	1	7	50	11	31
Br	98	0.002	-	1	250	6300	13.4	48

* "Oxid" refers to the chain-carrying radical in oxidations when $[O_2] / [RH] = 0$.

** E(ethane) is the activation energy in kcal $mole^{-1}$ for the abstraction of H· from ethane by the radical.

methyl, cyclopropyl, primary, secondary, and tertiary is observed, the reactivity increasing with decreasing bond strength. For the alkylperoxy and oxidation radicals it is notable that the C-H bond of cyclopropane is about eight times less reactive than a normal secondary bond, and the C-H in methane about ten times less reactive than a normal primary. Generally, it is observed that the differences between the relative reactivities of the C-H bonds decrease with increasing reactivity of the attacking radical.

There are at present no accurate data as to the amount of heat liberated in the formation of an alkylperoxy radical,

$$R + O_2 \longrightarrow ROO \qquad (7)$$

but Sleppy and Calvert[28] place the minimum at 5 kcal mole^{-1}, and suggest that it should be about 20 kcal mole^{-1} higher, Small and Ubbelohde[60] suggest it may be greater or equal to the heat liberated in the formation of a hydroperoxy radical[43]

$$H + O_2 \ (+M) \longrightarrow HO_2 \quad (+M), \ \Delta H \gtrsim 46 \text{ kcal mole} . \qquad (12)$$

However, due to the larger number of internal degrees of freedom in an alkylperoxy radical, the third body requirement is less stringent, except possibly for methylperoxy formation, and as a consequence, an energy rich radical is formed. In the oxidation of methyl radicals, recent work[24,25,27-29] suggests that with pressures of efficient third bodies (M) above 30 mm,

$$CH_3 + O_2 \ (+M) \longrightarrow CH_3OO \ (+M) \qquad (29)$$

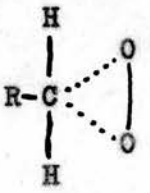
is the principal reaction. At lower third body pressures a second order reaction

$$CH_3 + O_2 \longrightarrow Y \qquad (30)$$

becomes increasingly important[24,25], competing with reaction (29).

Sleppy and Calvert[28] have not observed this effect but their third body pressures (neopentane + azomethane) were between 100 - 300 mm. Christie[25] did not specify the identity of Y, but Hoare and Walsh[24] believe it to be a methylperoxy radical with excess vibrational energy. It seems likely that a proportion of the methylperoxy radicals formed are energy rich, and that the fraction of energy rich radicals would depend upon total pressure and "efficient" third body pressure. The fraction of energy rich radicals should increase with the complexity of the alkyl radical, as more internal degrees of freedom will be available to absorb the excess energy. An alternate explanation of the fact that the rate of addition of alkyl radicals to oxygen is many times lower than the frequency of collision is that the reaction has a low probability factor[30,61].

If both normal and energy rich alkylperoxy radicals exist in the system, most of the hydrocarbon attack should be by the energy rich radicals. Small and Ubbelohde[60] suggest that the activated radical may be stabilized by bond tautomerism as it must undergo many collisions before reacting with a hydrocarbon. Form (b) should contribute with (a) if the O-C-O bond angle is about 70°.

(a) $RCH_2\text{-}O\text{-}O\cdot$ (b) 

Deactivation may occur either by energy transfer, or by chemical reaction[18,62], e.g.

$$Hg + ROO \longrightarrow HgO + RO \ .$$

Alternatively, if the lifetime of the alkylperoxy radical is long, a normal radical may become activated by collision and subsequently attack a hydrocarbon.

In the present experiments the overall rate of hydro-

carbon consumption was smaller for methylperoxy than for other alkylperoxy radicals, due to a lower proportion of energy rich radicals existing for this, the simplest, of the four alkylperoxy radicals. This qualitatively supports the hypothesis that the second order formation of active alkylperoxy radicals competes with a third order reaction yielding inactive radicals, and that the hydrocarbon attack is principally by energy rich radicals. The third order reaction is most important with simple radicals, i.e. $HO_2 > CH_3O_2$ etc.

It appears that even with copious initiation, an oxidation chain reaction will not occur at low temperatures. Badin[63] found no chains in the hydrogen atom initiated oxidation of alkanes. Small and Ubbelohde[18] found that when hydrocarbons were added to a rapidly reacting acetaldehyde-oxygen system at 150-250°, the hydrocarbons inhibited the overall reaction, and the alkylperoxy radicals formed from them were insufficiently reactive to propagate the chain. Burgess and Robb[64] found no evidence of a chain reaction below 250° in the mercury photosensitized oxidation of isobutane, which they believe to occur by a hydroperoxide chain mechanism. For normal paraffins (pentane, hexane, and heptane) they found a chain reaction, which they believed to be a hydroxyl radical chain giving ketones as products, starting some 100° lower. The temperature at which these chains commence increases with a decrease in the hydrocarbon length, and therefore, should be higher than 150° for n-butane and propane. In the present experiments at 230°, the rate of consumption of n-butane closely parallels that for isobutane, and there is no evidence of chain formation for alkylperoxy attack on isobutane. Since

$$\frac{\text{number of molecules of hydrocarbon consumed}}{\text{number of alkyl radicals produced}} \leq 0.6$$

chains cannot be important at the temperatures used for the alkylperoxy radical investigation. At these temperatures the probability of radical deactivation, and eventual destruction,

either homogeneously, or more likely at the walls, is high. However, the consumption of hydrocarbon at 230° is approximately five times that at 145° indicating that 230° is approaching the chain region where the chance of reaction is greater than that of deactivation. Paralleling this observation, Scheer and Taylor[32], in the azomethane photosensitized oxidation of propane, found no evidence of chains below 200°, rapid chains between 230-250°, and cool flames above 250°.

It is unlikely that the ROO-H bond strength is greatly different when R is an alkyl radical than when R is a hydrogen atom. If the currently accepted value[50] of D(HOO-H) = 89.5 kcal mole^{-1} is correct, the abstraction reactions (8) and (9) will be endothermic when RH is a saturated hydrocarbon. However, the activation energy in the gas phase need not be so great as the endothermicity of the reaction might predict, for the alkylperoxy radical attacking the hydrocarbon can carry with it some of its vibrational energy of formation[65]. If the older value[51] of 102 kcal mole^{-1} is accepted, the abstraction reaction will be exothermic and a low activation energy could be expected.

Since $E_{n\text{-butane}} - E_{propylene} = 3$ kcal mole^{-1}, the activation energy for hydrogen abstraction from saturated hydrocarbons by alkylperoxy radicals is approximately 3 kcal mole^{-1} greater than that for the consumption of olefins. Although the mechanism for the consumption of propylene is uncertain, it is improbable that it would have a negative activation energy ; therefore the minimum absolute activation energy for hydrogen abstraction from paraffins by alkylperoxy radicals is 3 kcal mole^{-1}.

The results in Table 20 show that the mean rate of consumption of hydrocarbon by alkylperoxy radicals at 230° is 5.1 times that at 145°. Since chaining at the higher temperature is unimportant, this factor of 5.1 is probably the change in the rate of attack by alkylperoxy radicals between these two temperatures. This change in rate corresponds to an activation energy of 8 kcal mole^{-1}.

Table 20

COMPARISON OF THE RATE OF HYDROCARBON CONSUMPTION BY ALKYLPEROXY RADICALS AT 145° AND 230°

Hydrocarbon Ratio	Attacking Radical	Rate of Hydrocarbon Consumption 145° (1.2×10^3 mm/min)*	230° (10^3 mm/min)	Consumption at 230° / Consumption at 145°
CYCLOPROPANE-ETHANE MIXTURES				
1:2	MeOO	12.6	31.8	2.5
2:1	MeOO	10.3	37.4	3.7
1:2	EtOO	10.2	72.5	7.1
2:1	EtOO	15.3	56.5	3.7
2:1	i-PrOO	20.3	144	7.1
2:1	t-BuOO	10.3	59.1	5.7
ETHANE-PROPANE MIXTURES				
3:1	MeOO	23.4	111	4.7
1:2	MeOO	35.7	157	4.4
3:1	EtOO	32.9	190	5.8
1:2	EtOO	46.6	313	6.7
PROPANE-ISOBUTANE MIXTURES				
3:1	MeOO	44.4	122	2.8
1:3	MeOO	46.1	148	3.2
3:1	EtOO	51.7	253	4.9
1:3	EtOO	52.5	320	6.1
1:1	i-PrOO	33.8	282	8.3
1:1	t-BuOO	26.2	80	3.1
PROPANE-n-BUTANE MIXTURES				
1:2	MeOO	54.5	229	4.2
1:2	EtOO	51.5	389	7.4
MEANS :	MeOO			3.7
	EtOO			6.0
	i-PrOO			7.7
	t-BuOO			4.4
	Overall			5.1

* The factor 1.2 here is to allow for more molecules being in the reaction vessel at a given pressure at the lower temperature.

The results for neopentane-propane mixtures have been omitted from the table because the intensities of illumination at the two temperatures were not the same. In other mixtures, the experimental conditions for individual runs are not strictly comparable, but the mean values listed in the table probably iron out most of the discrepencies except one : at 230º the illumination times are relatively short (approximately one-fifth those at 145º), and as a consequence the mean ketone concentration, and hence the radical concentration, will be lower at 145º. This effect will lower the rate of consumption at 145º. As the ratio of rates of consumption assumes equal radical concentrations, the ratios will be increased and give high values for the activation energy. Any slight chaining at 230º would also tend to make the activation energy high, and any contribtion to the activation energy for alkylperoxy attack by the activation energy of the formation reaction[28,30]

$$R + O_2 \longrightarrow ROO \quad (E_{act} = 0\text{-}1 \text{ kcal mole}^{-1}) \qquad (7)$$

will give a high value. Therefore, 8 kcal $mole^{-1}$ is a maximum value for the activation energy of the abstraction reaction.

The activation energies for the individual alkylperoxy radicals all fall in the range 6-10 kcal $mole^{-1}$, which is reasonable agreement in view of the discrepancies in the conditions of individual experiments.

From a comparison of radical reactivities with activation energies for attack on ethane (see Table 19), an activation energy for alkylperoxy attack of about 6 kcal $mole^{-1}$ can be deduced. At any rate, the value is not likely to be greater than that for methoxyl radicals, which are less reactive, so by analogy the maximum can be placed at 7-8 kcal $mole^{-1}$. This same maximum can be deduced for the activation energy of the chain-propagating reaction in the oxidation of saturated hydrocarbons in the initial stages.

Bateman[20] reports the activation energy for alkylperoxy attack on olefins in the liquid phase to be 6-13 kcal mole^{-1}, the higher values being for those olefins with stronger C-H bonds. Paraffins would be expected to have activation energies about 3 kcal mole^{-1} higher. However, the formation of energy rich alkylperoxy radicals in the liquid phase is less likely than in the gas phase, and deactivation of any excited species formed is more probable. A lowering of activation energy due to energy rich radicals is therefore unlikely to occur. If the activation energy depression effect proposed by Walsh[65] is several kilocalories, an activation energy of 6-8 kcal mole^{-1} for the abstraction reaction in the gas phase could be obtained.

This is considerably less than the 16 kcal mole^{-1} found by Burgess and Robb[64] for the overall activation energy of hydroperoxide chain mechanism in the mercury photosensitized oxidation of isobutane between 250° and 430°. For this value to be equal to the activation energy of the abstraction reaction, as the authors state, the mechanism which they propose would have to be essentially correct. It is undoubtedly an oversimplification, however, as it does not account for the large quantities of isobutene found in the oxidation of isobutane at these temperatures.

It can therefore be concluded that the activation energy for the abstraction of a hydrogen atom from a saturated hydrocarbon by an alkylperoxy radical lies between 3-8 kcal mole^{-1}. Although the A factors for these abstractions cannot be deduced absolutely from the present experiments, they are probably of the order of 10^8 l mole^{-1} sec^{-1} usual for the reactions of small radicals[59]. They are at any rate similar for all hydrocarbons, as the ratios of A factors determined from the Arrhenius plots are close to unity.

CONCLUSION

This study indicates that the important chain-propagating radicals in the oxidation of saturated hydrocarbons are of the type ROO· in the initial stages of oxidation at all temperatures between 145-500°, and throughout the oxidation at temperatures below 350°.

Below the normal temperatures of thermal oxidations, initial attack on a saturated hydrocarbon undergoing oxidation appears to be by an alkylperoxy radical possessing excess vibrational energy. In this region oxidation occurs by a non-chain mechanism, and hydroperoxides are the principal products ; olefins are not formed.

The experimental evidence presented here suggests that as the temperature region of thermal oxidations is reached, a chain propagated by HO_2 radicals supercedes alkylperoxy radical abstraction as the principal medium for hydrocarbon consumption. Considerable independent evidence exists in support of HO_2 radical chains, and it seems probable that the following reactions are mainly responsible for the consumption of saturated hydrocarbons undergoing oxidation in the initial stages of reaction,

$$RH + HO_2 \longrightarrow R\cdot + H_2O_2 \qquad (13)$$

$$R\cdot + O_2 \longrightarrow \text{olefin} + HO_2 \qquad (10)$$

At higher temperatures, above about 350°, the chain mechanism appears to be more complex, and at least two chain-propagating reactions operate, depending upon the degree of advancement of the reaction. The HO_2 chain mechanism still predominates in the initial stages, and possibly is important to some extent throughout the reaction. However, a second chain-propagating radical becomes increasingly important as the

reaction proceeds. Although the identity of this radical is uncertain, it seems likely that it is OH . The reactivity of OH qualitatively fits that of the later stage oxidation radical, and OH could be formed by the secondary oxidation of some primary product.

The relative rates of attack at different points in paraffins by alkylperoxy radicals and by the chain-propagating radical in the initial stages of oxidation that have been calculated from the experimental data are in keeping with those for attack by other radicals. Initial attack occurs at tertiary bonds in preference to secondary, and secondary in preference to primary. The C-H bonds in cyclopropane are about eight times less reactive than normal secondary bonds ; those in methane at least ten times less reactive than normal primary bonds at 230°.

The activation energy for the abstraction of a hydrogen atom from a saturated hydrocarbon by an alkylperoxy radical is 3-8 kcal $mole^{-1}$. The close resemblence between the relative rates of hydrocarbon consumption by the chain-propagating reactions in oxidations at zero oxygen concentration and by alkylperoxy radical reactions suggests that reaction (13)

$$RH + HO_2 \longrightarrow R + H_2O_2 \qquad (13)$$

will have this same activation energy. The activation energy differences between abstraction reactions from various hydrocarbons are small, as the small absolute activation energies suggest.

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